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CRYSTALS

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THE VIBRATION SPECTRA OF CRYSTALS

Part I. Basic Theory

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1. Introduction

A knowledge of the modes and frequencies of vibration of the atoms in a crystal about their positions of equilibrium is of the utmost significance for the theory of the solid state. For, such knowledge is complementary to that regarding the structure of the solid furnished by the data of X-ray and electron diffraction. These latter data enable the geometric positions of the atoms to be ascertained, while the modes and frequencies of atomic vibration permit of the evaluation of the forces which hold them together as a rigid structure. The study and interpretation of the vibration spectra of crystals is thus the pathway to a fuller understanding of the nature of the solid state and the elucidation of the physical properties of solids generally. It follows that the theory of these spectra is a topic of outstanding importance for the progress of crystal physics.

The problem of finding the nature of the vibration spectrum of a crystal may be approached from two different points of view. The first is that which bases itself on the known behaviour of elastic solids. Acoustic theory and experience alike indicate that a solid body has a whole series of normal modes of vibration determined by its external form and dimensions. These may be regarded as stationary vibration patterns resulting from the interference of elastic waves which traverse the interior of the solid in different directions and suffer reflections at its outer boundary. On this view, the frequencies of the modes would be determined by the length of the waves and their type. The problem of enumerating the possible stationary vibrations and of arranging them in a frequency scale is somewhat more complicated than the analogous problem for an enclosed volume of fluid, since

there are three types of waves instead of one as in the latter case, and since the wave-velocities in a crystal also depend on the direction of propagation. It is evident, however, that the general nature of the results would be similar in the two cases. There would be a crowding together of the modes as the wave-lengths are diminished and the frequencies of vibration are correspondingly greater, their number becoming ultimately very large. Hence, the vibration spectrum would to all intents and purposes be a continuous one. It may be remarked that the method of enumeration of the vibrational modes in this manner according to wave-lengths or frequencies does not in any way compel us to take account of the discrete structure of the medium and in effect regards the latter as a continuum.

The second point of view from which the subject may be approached is that in which we fix our attention on the movements of the individual atoms in the solid. The structure of a crystal is built up of a great number of units of very small size, all of which are exactly alike and each of which comprises a finite number of atoms. Since the range of the interatomic forces is also very small, the problem of finding the possible modes of vibration of these groups of atoms is of the same general nature as that of finding the normal modes of vibration of a polyatomic molecule. The nature of the results to be expected would therefore also be similar, and the vibration spectrum of a crystal should accordingly consist of a finite set of sharply defined frequencies, each of which represents an exactly specifiable mode of vibration. The characteristic frequencies would be the same for every one of the vibrating groups of atoms, and hence in relation to the entire crystal must be considered as being highly degenerate.

Thus, the continuum standpoint and the atomistic standpoint lead to conceptions of the nature of the vibration spectrum of a crystal which are radically different from each other. The two points of view are therefore mutually exclusive, and since they both appear reasonable, we infer that the ranges of frequency in which they are respectively appropriate are quite different. The continuum standpoint is the one which would naturally be adopted in considering the lower part of the frequency range comprised in the spectrum, while the atomistic standpoint is obviously the correct one to take up when we are concerned with the upper part of the frequency range. In other words, the vibration spectrum of every crystal is composed of two parts which are essentially different in nature, namely the atomic vibration spectrum properly so called which exhibits a discrete set of monochromatic frequencies appearing in the infra-red, and the elastic spectrum which is continuous and forms a low-frequency appendage to it.

The present paper has a two-fold purpose. In the first part, we shall present a theoretical discussion of the problem and justify the statements made above concerning the nature of the vibration spectra of crystals. The arguments put forward are simpler without being less rigorous than those contained in an earlier presentation of this topic (Raman, 1943). In the later parts, we shall review the experimental data for the spectroscopic behaviour of crystals as known at the present time and show that the facts are in complete accord with the theoretical ideas developed in the first part. Incidentally, we shall also comment upon the older theories of the subject which lead to the conclusion that the vibration spectrum of a crystal is a continuous one throughout the entire range of frequency. It will be shown that these theories are based on an extrapolation of the ideas derived from elastic solid behaviour into the atomistic field, and that such extrapolation is invalid and leads to results which are contradicted by the experimental facts.

2. The Eigenvibrations of Crystal Structures

The structure of a crystal consists of a great number of similar and similarly situated cells each containing the same number of atoms, and the clue to the spectroscopic behaviour of the crystal is therefore to be found in the properties of the group of atoms contained in the unit cell. In other words, we have to consider the possible modes of vibration of the group of atoms included in the unit cell, and the problem is therefore generally analogous to the theory of vibrations of polyatomic molecules. There is however a notable difference between the two cases arising from the fact that the atoms in the unit cell are not isolated from the rest of the crystal; it is clearly necessary to take account of the interactions with the surrounding cells in so far as they affect the motion of the atoms in the cell under consideration. The frequencies of vibration with which we are concerned lie in the infra-red. Hence, the problem does not lie strictly within the scope of the classical mechanics. Nevertheless, as in the case of polyatomic molecules, we may hope that the methods of classical mechanics suffice to yield results which are in agreement with the facts in all essential respects. Also, as in the case of polyatomic molecules, we may in the first instance limit ourselves to the theory of small vibrations under harmonic forces. The modifications arising from the removal of these restrictions are, however, by no means unimportant. They will be dealt with later in the paper.

In any eigenvibration of the atoms contained in the unit cell, their frequencies of vibration are necessarily the same, while the phases are all the same or opposite. In considering the interactions with the surrounding atoms, we may properly assume that this is true also for the atoms included

in the surrounding cells whose direct interactions with the unit cell under consideration are of sensible magnitude. We proceed to find the cases for which these requirements are satisfied.

The equations of motion of the atoms in a crystal for an oscillation proportional to sin ωt take the general form

$$m_k \xi_{kr} \omega^2 = \sum_s \sum_l \sum_\eta F^{\xi k r}_{\eta l s} \cdot \eta_{ls} \qquad (1)$$

Here, m denotes the mass of an atom, while the co-ordinates ξ, η, ζ indicate its displacements parallel to x, y and z respectively. The suffixes k and l indicate particular atoms in the unit cell, where the suffixes r and s refer to particular cells of the lattice in which the atoms are situated. F denotes a force-factor, its upper and lower suffixes indicating respectively the displacement of the particular atom on which it acts and the displacement of the particular atom giving rise to the force. The triple summation must be made over the ξ, η and ζ values of all the atoms in the crystal for which the force-factors are not negligible in respect of the particular atom under consideration; the size of the domain including all such atoms would depend on the range of the interatomic forces. We shall assume the crystal to be of sufficient size to ensure that its external boundary is very remote from the limits of such domain. To enable us to solve the set of $3p$ equations of motion of the p atoms comprised in the unit cell under consideration, we shall require to know the displacements of the atoms in the neighbouring cells which also appear on the right-hand side of the equations (1). To enable them to be found, we make use of the fact that in any eigenvibration, the equations of motion of the atoms included in these cells must also simultaneously be satisfied. Considering the atoms comprised in a cell adjacent to the rth which we denote as the $(r+1)$th, their equations of motion would have the form

$$m_k \xi_{k(r+1)} \omega^2 = \sum_s \sum_l \sum_\eta \cdot F^{\xi k (r+1)}_{\eta l (s+1)} \cdot \eta_{l(s+1)} \qquad (2)$$

the cell index $(s+1)$ representing one adjacent to the cell of index s along the same axis is as that on which the rth and $(r+1)$th cells are situated.

Now the transitional symmetry of the crystal has the consequence that the force-constants for adjacent cells satisfy general relations of the form

$$F^{\xi k r}_{\eta l s} = F^{\xi k (r+1)}_{\eta l (s+1)} \qquad (3)$$

Comparing equations (1) and (2) and taking account of the relations given by (3), we notice that provided general relations subsist connecting the displacement of equivalent atoms which are

either of the form

$$\xi_{kr} = \xi_{k\,(r+1)} \text{ and } \eta_{ls} = \eta_{l\,(s+1)} \tag{4}$$

or of the form

$$\xi_{kr} = -\xi_{k\,(r+1)} \text{ and } \eta_{ls} = -\eta_{l\,(s+1)} \tag{5}$$

the $3p$ equations (1) and the corresponding $3p$ equations (2) would become identical. In these circumstances, any set of displacement co-ordinates which satisfy the former set of equations would also satisfy the latter. Further, the number of unknown co-ordinates appearing in the $3p$ equations (1) would be reduced to $3p$ only by reason of (4) or (5), thus enabling them to be completely solved. However, (4) and (5) being different alternatives, the $3p$ equations obtained by making use of these relations would be different, and the solutions obtained would also be different. Further, there would be two such alternatives in respect of the cells adjacent to each other along each of the three axes of the lattice, and these three sets of alternative possibilities would be independent of each other, so that there would be $2 \times 2 \times 2$ or 8 sets of alternative possibilities to be considered. Each of these would, in general, give a different set of $3p$ equations and therefore a different set of solutions. Thus, in all, we would obtain $24p$ solutions on the basis of the relations indicated by (4) and (5) above.

We shall now consider the significance of the alternative relations (4) and (5) which we have assumed to subsist in order to enable the equations of motion to be reduced and solved. They evidently signify that *the amplitudes of vibration of equivalent atoms in the different cells are the same, while their phases are either all the same or else alternate in successive cells along each of the three axes of the lattice.* In either case, the energy of vibration is the same in the different cells of the lattice when the frequency is the same. It is obvious that such a state of affairs necessarily represents a possible stationary regime within the crystal. In other words, the $24p$ solutions of the equations of motion obtained on this basis represent the normal modes of vibration of the crystal structure. It will be noticed that only in $3p$ solutions would the phase of the vibration be the same in all the cells of the lattice; in the remaining $21p$ solutions, the phase of the vibration is opposite in adjacent cells of the lattice along one, two or all three of its axes. In these latter, the condition that the centre of inertia of the system should remain at rest is automatically secured. The constraints necessary to secure the same condition would however reduce the $3p$ solutions of the former kind to $(3p - 3)$ solutions, so that in all we would have $(24p - 3)$ eigenvibrations and not $24p$.

It will be noticed that if we mark out domains in the crystal which extend in each direction twice as much as the unit cells of the lattice, the pattern of vibration within each such domain would be the same as for neighbouring ones in each of the $(24p - 3)$ modes of vibration indicated by the preceding argument. *Hence, the results of that argument may be summarised by the statement that the units of the vibration pattern of the crystal are super-cells having twice the linear dimensions and therefore eight times the volume of the static units of the crystal structure.* The number of atoms included in each such dynamic unit or super-cell is $8p$, and we may therefore regard the $(24p - 3)$ modes as its internal vibrations and the three excluded degrees of freedom as its three translations. This point of view is useful in two ways. Firstly, it indicates that in relation to the entire crystal, *each of our* $(24p - 3)$ *modes of vibration is highly degenerate, being in fact N-fold degenerate if N be the number of super-cells contained in the crystal.* Secondly, the three excluded degrees of freedom which represent the translations of the super-cell provide an appropriate starting point for a consideration of the possible elastic modes of vibrations of the solid. We shall return to this aspect of the subject later in the paper.

3. Some Illustrative Examples

As an illustration of the general theory set out above, we shall now consider two specific cases, *viz.*, that of a face-centred cubic lattice of atoms, as also the structure resulting from the interpenetration of two such lattices, *viz.*, that of diamond or zinc-blende and describe their characteristic modes of vibration.

The unit cells in a face-centred cubic lattice are really rhombohedra, the unit translations being those by which an atom placed at the corner of the cube goes over respectively to the three neighbouring face-centred atoms. The theorem that equivalent atoms in the lattice have the same amplitude of vibration and either the same phase or the opposite phases successively along the axes of the lattice enables us immediately to describe the possible modes. An atom located at a cube corner and the three others located at the nearest face-centres form the four vertices of a regular tetrahedron the faces of which are the (111) planes, while its diagonal planes are the (100) planes of atoms in the crystal. It is easily seen that all the eigenvibrations are movements of these planes of atoms; alternate planes move in opposite phases, while the directions of movement are indicated by considerations of symmetry to be either normal or tangential to the respective planes. Thus, there are only four different kinds of vibration of the lattice, namely the normal and tangential vibrations respectively of the octahedral and cubic

planes of atoms, the tangential vibrations being twice as many as the normal ones. As there are four sets of octahedral planes and three sets of cubic planes in the lattice, the four species of vibration have degeneracies of 4, 8, 3 and 6 respectively, making up a total of 21 modes. Adding the 3 translations of the super-lattice cell, we obtain the total of 24 degrees of freedom of the 8 atoms contained in it.

The possible modes of vibration of the diamond or zinc-blende structure may be obtained by coupling similar modes of vibration of the two face-centred lattices as described above with appropriate relations of amplitude and phase. There are only two possibilities, *viz.*, that the oscillations of the planes of atoms adjacent to each other belonging respectively to the two lattices are in the same or the opposite phase. Hence, the four types of eigenvibration of a face-centred cubic lattice give us eight types of vibration of the structure. To this, we must add a ninth mode of vibration representing the translations in opposite phases of the two lattices with respect to each other. Thus in all, we have 9 modes with degeneracies 4, 4, 8, 8, 3, 3, 6, 6 and 3 respectively, making up a total of 45 degrees of freedom. The 3 translations of the two lattices moving together in the same phase are excluded from this scheme. Taking account of them, we recover the 48 degrees of freedom of the 16 atoms included in the super-lattice cell.

4. The Elastic Vibration Spectrum

We now turn to a consideration of the problem from the point of view provided by the theory of the vibrations of elastic solids. The principles on which an enumeration of the possible modes of vibration of an elastic solid may be based are indicated by the comparatively simpler problem of the vibrations of an enclosed volume of fluid. Considering a rectangular chamber whose edge-lengths are α, β, γ respectively, it may be shown either directly or by application of Fourier's theorem that the general solution which includes all particular solutions of the equations of wave-motion satisfying the boundary conditions at the walls of the enclosure is

$$\phi = \Sigma\Sigma\Sigma\,(\mathrm{A}\cos kat + \mathrm{B}\sin kat) \times \cos\frac{n_1\pi x}{\alpha}\cos\frac{n_2\pi y}{\beta}\cos\frac{n_3\pi z}{\gamma}, \tag{6}$$

where ϕ is the velocity-potential, A and B are arbitrary constants, while n_1, n_2, n_3 are positive integers and k is $2\pi/\lambda$, where λ is the "wave-length" of the stationary vibration. It is defined by the relation

$$k^2 = \pi^2\,(n_1^2/\alpha^2 + n_2^2/\beta^2 + n_3^2/\gamma^2) \tag{7}$$

and hence λ diminishes as n_1, n_2, n_3 are increased. If the medium be regarded as continuous, n_1, n_2, n_3 may be as large as we please, and the number of possible stationary wave-patterns is then unlimited. We may, however, if we so desire, set a limit to the total number of possible stationary patterns of vibration by assuming that the maximum possible values of n_1, n_2, n_3 are respectively N_1, N_2, N_3. The total number of possible eigenvibrations is then the product $N_1N_2N_3$.

Equation (7) connects the "wave-length" of an oscillation with the linear dimensions of the vibrating body and the number of parts of its aliquot division by the resulting vibration in each of three mutually orthogonal directions. We shall not be wholly at fault in assuming a similar relationship to subsist in the case of the elastic vibrations of a rectangular block of solid. Earlier in the paper, we have seen that the atomistic approach to our problem leads to the result that the structure of a crystal has $(24p - 3)$ characteristic modes of vibration, and we identified these with the internal vibrations of a group of $8p$ atoms included in a super-lattice cell having twice the linear dimensions and hence eight times the volume of the unit cell of the crystal lattice. The three excluded degrees of freedom on the same basis represent the three translations of the super-cell, and if there be N such super-cells comprised in the entire crystal, we have 3N degrees of dynamical freedom of movement which are left unaccounted for in the atomistic treatment. In view of the remarks made in the introduction, we may properly identify these with the total number of possible elastic eigenvibrations of the crystal. Since there are three types of elastic waves in a crystal, we may ascribe one-third of the total number to each of the corresponding types of elastic eigenvibration. Accordingly, on the basis of the foregoing argument, we set

$$N = N_1N_2N_3 \tag{8}$$

which signifies merely that the total number of elastic eigenvibrations of each type is the same as the total number of super-lattice cells comprised in the crystal. By virtue of (8), we may write (7) in the form

$$4/\lambda^2 = (n_1^2/N_1^2 \cdot 1/d_1^2 + n_2^2/N_2^2 \cdot 1/d_2^2 + n_3^2/N_3^2 \cdot 1/d_3^2) \tag{9}$$

which connects the reciprocal of the wave-length λ of the vibration with the reciprocals of certain spacings d_1, d_2, d_3 whose product $d_1d_2d_3$ is equal to the volume of the super-lattice cell. As N_1, N_2, N_3 are very large numbers, the wave-lengths permitted by (9) form a practically continuous sequence of values which become densely crowded together as n_1, n_2, n_3 approach their maximum possible values N_1, N_2, N_3. When one of the three numbers n_1, n_2, n_3 has its maximum value and the other two are set equal to zero,

λ becomes equal to $2d_1$ or $2d_2$ or $2d_3$ respectively. Thus, the " limiting wave-lengths " along the three edges of the rectangular block are related in a very simple manner to the linear dimensions of the super-lattice cell of the crystal structure. In the particular case where the edges of the block are parallel to the axes of the crystal lattice, *the limiting wave-lengths are just twice the edges of the super-lattice cell or four times the edges of the lattice cell of the crystal. Vice-versa,* if the limiting wave-lengths of the elastic eigenvibrations are so chosen as to satisfy these relations, *the number of degrees of dynamical freedom left out from the atomistic enumeration of the vibrations in the crystal are completely accounted for as its elastic eigenvibrations.* It will be noticed that we are *not* assuming $d_1 = d_2 = d_3$, and hence the argument is not limited to the case of cubic symmetry but is more general. In passing from an enumeration of the eigenvibrations on the scale of wave-lengths provided by (9) to an enumeration on a scale of frequencies, we must, of course, take account of the fact that the ratio of wave-length to frequency is different for the three types of elastic waves and is also a function of the direction of propagation.

We may illustrate the preceding argument by considering once again the case of a face-centred cubic lattice. As mentioned earlier, the eigenvibrations of such a lattice are of four different kinds which may be described as being respectively normal and tangential oscillations of the cubic and octahedral planes of atoms, the movements of alternate planes of atoms being in opposite phases. The normal oscillations of the cubic planes are represented in Fig. 1. A similar figure with the arrows parallel to the atomic

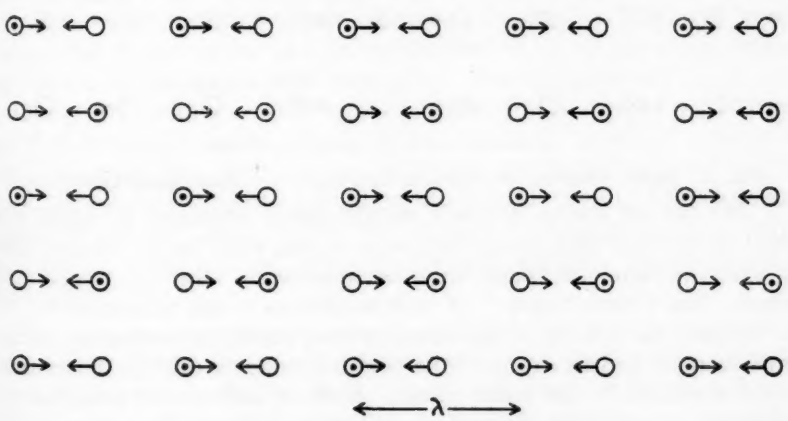

FIG. 1. Eigenvibrations of a Face-centred Cubic Lattice

planes would represent the tangential oscillations. With an altered spacing of the planes the figure would also represent the oscillations of the octahedral layers of atoms.

As will be seen from the figure, there are no nodal planes or layers of atoms at rest, and since the nature of the vibration is completely determined by the lattice structure, the mode is a characteristic property of that structure and not an elastic vibration properly so called. Since, however, the motion repeats itself periodically along the crystal axes, we may ascribe to it a "wave-length" which as seen from the figure is *twice* the distance between the atomic layers. Fig. 2 represents an elastic vibration properly so-called with the smallest possible wave-length; every alternate layer of atoms is a nodal plane which remains at rest, while the intervening planes of atoms move in opposite phases. The "wave-length" is thus four times the distance between the atomic layers. A similar figure with the arrows parallel to the atomic planes would represent the transverse elastic vibration of smallest wave-length.

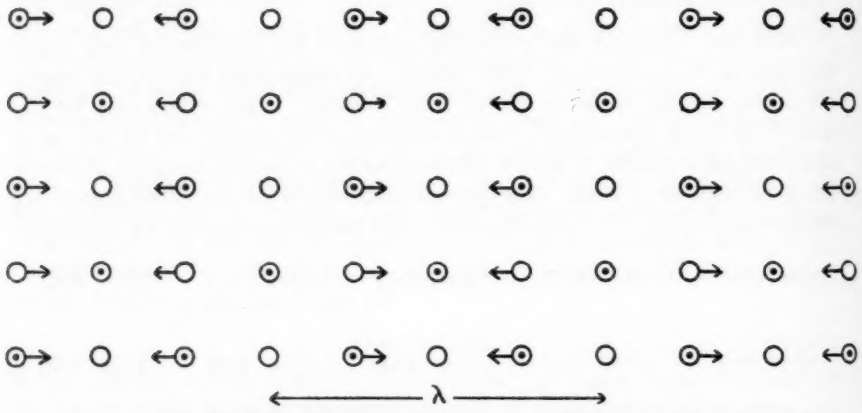

FIG. 2. Elastic Vibrations of Minimum Wave-length in a Face-centred Cubic Lattice

We can, of course, similarly picture elastic vibrations in which every third or fourth or fifth plane of atoms is at rest, while the intervening planes of atoms oscillate with phases which are opposite on either side of each nodal plane. The "wave-lengths" of such oscillations would be respectively 6, 8 or 10 times the spacing of the atomic planes, the motion repeating itself at these intervals and the energy of the vibration being the same in the successive layers separated by the nodal planes. Such an arithmetical progression of increasing wave-lengths is however altogether different from that contemplated by equation (9) above in which they form a densely crowded sequence

with wave-lengths diminishing in harmonic progression, the permitted values being determined by aliquot division of the macroscopic dimensions of the solid. Moreover, the form and disposition of the nodal planes of elastic vibration are determined by the shape and dimensions of the outer boundary of the solid and not by its internal structure. Hence, having set the lower limit of wave-length at four times the lattice spacings, we must for all larger wave-lengths and therefore lower frequencies of elastic vibration ignore the discrete structure of the solid and treat it as a continuum. *Per contra*, we are precluded from extending into the region of the higher frequencies of vibration a treatment based on the idea of free propagation of elastic waves of lengths determined by the external dimensions of the solid.

5. Remarks on Some Earlier Theories

The Debye Theory.—The foregoing remarks prepare us for a consideration of the earlier theories of the vibration spectra of crystals. The prototype of these theories is Debye's well-known treatment (1912) of the specific heat problem for elementary solids. This is based on the postulate that the thermal agitation in a solid may be identified with stationary elastic vibrations in it of various wave-lengths superposed on each other. All the three possible kinds of elastic vibration are assumed to have frequencies inversely proportional to their respective wave-lengths and to terminate at a common upper limit of frequency. The simplicity of the Debye formula for the specific heat is a consequence of these specific assumptions. Later writers have sought to modify the theory by postulating that all the three types of elastic vibration (one longitudinal and two transverse) have a common upper limit of wave-length instead of frequency. With this modification, the Debye theory and the results derived in the preceding section may be readily compared with each other. Limiting ourselves to the case in which each cell of the crystal lattice contains only one atom, it is obvious that if all the possible atomic vibrations are considered as elastic eigenvibrations, they would be eight times more numerous, and the limiting wave-lengths would be one-half of those derived in the present paper. The additional eigenvibrations are those having the smallest wave-lengths and therefore the highest frequencies, and they form the great majority, *viz.*, seven out of every eight.

In order to appreciate the precise nature of the situation thus arising, we consider the specific case of a face-centred cubic lattice. Figs. 1 and 2 above show respectively the characteristic eigenvibrations of the structure and the elastic vibrations of minimum wave-length possible in it according to our present point of view. It is evident that the great majority of the

stationary vibrations assumed by the Debye theory (seven-eighths of the total number) would have "wave-lengths" intermediate between those represented by these two figures. We may remark, however, that a characteristic feature of stationary vibrations in a continuous elastic medium—*vide* equation (6) of the preceding section—is that the medium is partitioned by the nodal planes into cells in which the energy of oscillation is the same and the phase opposite in alternate cells. The same situation in the case of a discontinuous periodic structure is represented in Figs. 1 and 2, but there is clearly no possibility of a stationary vibration with these characters and of wave-length intermediate between twice and four times the atomic spacing. We can, of course, postulate waves of any intermediate wave-length that we may choose and assume them to traverse the discontinuous periodic structure in opposite directions. But the result of their superposition would in no way resemble the stationary vibrations described in equation (6) which form the basis of the enumeration, since the energy of the vibration would fluctuate arbitrarily along the direction of propagation. The situation is thus that *the overwhelming majority of the stationary modes of vibration which are assumed to exist in Debye's theory are possible only in an elastic continuum but have no counterparts in a periodically stratified structure.* In other words, the Debye theory is based on an extrapolation of notions derived from the behaviour of elastic solids into the field of atomic theory, such extrapolation being, on the face of it, physically untenable. The postulates made in the theory are therefore invalid even in the case of crystals of the simplest structure to which the foregoing discussion has been limited.

The Born-Karman Theory.—We now proceed to comment on the so-called lattice dynamics of Born and Karman. This claims to be more exact than the Debye theory and also to include within its scope crystals of complex structure comprising two or more atoms in each lattice cell. For this purpose, the theory (1923) divides the degrees of freedom of the system—namely thrice the total number of atoms—into distinct groups which are each equal to the number of lattice cells comprised in the crystal. Each degree of freedom corresponds to a wave which is assumed to traverse the crystal, and we have thus present in it an immense number of sets of waves of different wave-lengths, each set corresponding to a group of wave-lengths chosen and allotted on the same common plan. $(3p - 3)$ of the groups of waves represent the so-called "optical" vibrations of the lattice, while the remaining 3 groups represent its "acoustic vibrations". The frequencies of vibration depend on the wave-lengths, and each group accordingly represents an immense number of different frequencies of vibration. The nature of the vibration spectrum has to be determined by calculation on the

basis of specific assumptions regarding the nature and magnitude of the interatomic forces. As the computations are laborious, it is not surprising that comparatively few cases have actually been worked out in detail. The published results, however, indicate that the vibration spectra in both the "optical" and the "acoustic" branches are diffuse continua which overlap each other (Blackman, 1935; Kellermann, 1940). Such a result might have been expected *a priori* in view of the assumptions underlying the theory. For the "wave-lengths" assumed are most crowded together when they are smallest and are most nearly comparable with the lattice spacings of the crystal. The "optical frequencies" depend notably on the wave-lengths when these are small, and hence the assumed distribution of wave-lengths results in spreading out the "optical spectrum" into a diffuse continuum, instead of its being a set of sharply defined lines as in the case of vibration spectra of polyatomic molecules.

The Born-Karman theory rests on the premise that a crystal has as many different frequencies of vibration as it has degrees of dynamical freedom, and the sets of waves with which its vibrations are identified are indeed assumed to secure this result. Neither the premise nor the assumptions made to ensure its fulfilment can, however, be justified. As has been remarked earlier in the paper, a crystal consists of an immense number of similar groups of atoms whose characteristic modes of vibration are necessarily all similar, and hence a high degree of degeneracy is necessarily to be expected in respect of the vibration frequencies of the system. Further, *a wave is not a normal vibration since the phase changes progressively along its course.* Hence, an enumeration of waves is not a valid procedure unless it can be shown that a physical mechanism exists which selects particular wave-lengths and transforms the motion to normal vibrations of a determinate type. Such a mechanism exists in respect of the elastic vibrations, being provided by the reflection of the waves at the boundaries of the crystal and the consequent formation of wave-patterns of a determinate type by interference. But as we have seen above, stationary wave-patterns of this kind can account for only a small proportion of the dynamical degrees of freedom even in the case of crystals of simple type having only one atom in each lattice cell. It follows that in the case of crystals of complex structure, the proportion of the dynamical degrees of freedom represented by stationary wave-patterns would be even smaller. Hence, the identification of the socalled "optical vibrations" with waves having the same set of wave-lengths as the elastic vibrations has no physical meaning or justification. In effect, the Born-Karman theory ascribes to the atomic structure of a crystal an immense number of modes and frequencies of vibration which it does not really possess.

6. Molecular Crystals

The arguments and results set out in Section 2 above are, of course, quite general, and do not depend on the particular manner in which the p atoms in the unit cell of the crystal are linked with each other or with the atoms in the neighbouring cells. Some of them, for instance, may be constituent parts of ions or molecules, *e.g.*, the CO_3 ions in calcite or the $C_{10}H_8$ molecules in a naphthalene crystal. Indeed, it is precisely such cases which make it most obvious that the vibration spectra of crystals in the infra-red should consist of a sharply defined set of monochromatic frequencies and not a diffuse continuum. For, we know that the ions or molecules in the free state have sharply defined spectral frequencies; though their mutual interactions in a crystal would have to be considered, these interactions are exactly specifiable and hence could only result in altering the vibration frequencies and increasing their number without changing the essential nature of the spectra. To show that this is the case, we may consider the particular example of a crystal in which the p atoms in each lattice cell form a single molecule. Each such molecule has $3p$ degrees of dynamical freedom which may be identified with specific modes of vibration in the crystal, since simple rotations and translations are excluded, at least ordinarily. The nature of a normal vibration, *viz.*, that all the particles in the system vibrate with the same frequency and with the same or opposite phases enables us to define the manner in which the vibrations of the interacting molecules would be related to each other. Since every molecule vibrates with the same frequency as its neighbours, the forces which come into play must be the same for all. These forces include not only the internal ones arising within each molecule but also the forces of interaction between them. Hence, the latter should also be the same for all molecules. But the forces of interaction are determined by the amplitudes and phases of vibration. Hence, to ensure that the forces of interaction are the same, it is necessary that the molecules which interact with each other vibrate with the same amplitude, while each molecule has the same relation of phase to its neighbours that every other molecule has. The latter requirement can only be satisfied if the phases are either all the same or else alternate in successive cells of the lattice along one, two, or all three of its axes. We have thus $2 \times 2 \times 2$ or 8 different ways in which the requirements for a normal vibration may be satisfied. Hence, each of the $3p$ possible modes of vibration of a molecule would be modified in 8 different ways, giving us in all $24p$ different normal vibrations, which is the same result as that deduced in Section 2, if we exclude the 3 translations of the molecules moving together as a group.

The foregoing approach to the subject is useful in elucidating the relations between the vibration spectrum of a crystal and the spectra of the same substance in the liquid and gaseous conditions. The $(24p-3)$ modes of vibration may be divided into two classes, namely, $(3p-3)$ modes in which the amplitude and phase of the vibration of a molecule are the same as those of its neighbours, and $21p$ modes in which the vibration occurs in opposite phase in alternate layers of the crystal structure. The $(3p-3)$ modes of the first kind represent the internal vibrations and the rotational oscillations of the molecules, while the $21p$ modes of the second kind would include also the 21 modes of translational oscillation of the molecules against each other. Unless the forces of interaction are large, the internal oscillations of the second kind would differ but little in frequency from similar oscillations of the first kind, and both would be nearly the same as for the free molecules. On the other hand, the rotational oscillations with discrete frequencies which are characteristic of the crystal are determined entirely by the interactions between the molecules, and hence they should differ notably in the first and second class of normal modes.

7. Anharmonicity and Interaction of Vibrations

So far, we have concerned ourselves with small oscillations under harmonic forces. In the actual problem, the amplitudes of vibration are determined by quantum-theoretical considerations and are by no means infinitesimal. Hence, a complete theory would require us to include, in addition to the forces proportional to the atomic displacements, also forces proportional to their squares and to their products. On introducing such additional terms into the equations, it becomes evident that the motion can no longer be described as a summation of independent normal vibrations and that interactions would arise profoundly modifying the dynamical behaviour of the system. Problems of this kind have already been considered in the theory of the vibrations of polyatomic molecules (Herzberg, 1945), and we may therefore take over the known results of that theory *mutatis mutandis* in our present case. If the anharmonicity be not too large, the behaviour of the system may still be described by sets of quantum numbers, each set corresponding to one of the normal vibrations possible in the harmonic approximation. The quantum numbers do not, however, as in the harmonic case, represent equal increments of energy, but a diminishing sequence of increments. The selection rules are also modified and in particular, overtones and combinational frequencies forbidden in the harmonic approximation are permitted to appear. Overtones and combinations may also appear by reason of the electric moments associated with the vibrations having a non-linear dependence on the amplitudes. Anharmonicity results

further in cases of non-accidental degeneracy in the splitting up of various higher energy levels which would be coincident in the harmonic approximation. Accidental degeneracy may also result in splitting up or displacing the energy levels concerned and in modifying the intensities with which they appear in the spectra.

8. Influence of Temperature

Anharmonicity also plays an important role when we consider the effect of elevating the temperature of a crystal on its vibration spectrum. As the temperature rises, a considerable proportion of the various low-lying energy levels would be thermally excited, as also a smaller proportion of the higher ones. Hence, any further excitation caused, for instance, by the incidence of radiation on the crystal has to start from the thermally excited levels, and by reason of the anharmonicity, the energy increments would then be less than for similar transitions from the ground state. As a consequence, the spectral lines corresponding to various possibilities which are equivalent in the harmonic approximation would no longer be coincident. The effect of elevating the temperature would accordingly be to lower the vibrational frequencies and simultaneously to spread them out over a finite range of values. Further, since the majority of the induced transitions start from the thermally excited levels and not from the ground state, the electrical anharmonicity would also come into play and make the observed intensity of the lines less than what they would be if there were no such anharmonicity.

It is evident that similar results would also follow from the interaction between the eigenvibrations of the crystal structure and the elastic vibrations of the solid. The energy of an elastic vibration is distributed over the entire volume of the crystal, and hence its amplitude would be exceedingly small. Hence, the elastic vibrations, considered individually, would have no sensible perturbing effect on the eigenvibrations. The position would however, be altered if we consider the aggregate effect of all the elastic modes of vibration when thermally excited, since their number is very large. A convenient way of regarding the matter is to fix our attention on a very small element of volume in the crystal. This volume element would, as the result of the thermal agitation, suffer fluctuations of density. These may be regarded as oscillations of varying amplitude and frequency. When the volume element considered is sufficiently small, the density fluctuations would be large enough to perturb the eigenfrequencies to an observable extent, lowering them and spreading them out over a finite range of values.

6. Summary

The paper presents the author's theory of the vibration spectra of crystals from a fresh point of view. It is shown that the nature of the spectra is necessarily different in the two regions of frequency in which they represent respectively the characteristic eigenvibrations of the crystal structure and the stationary wave-patterns of elastic vibration. The eigenvibrations repeat themselves in volume elements within the crystal having twice the linear dimensions and eight times the volume of the lattice cells. The number of modes of eigenvibration is $(24p-3)$, p being the number of atoms in each lattice cell. The spectral frequencies which are $(24p-3)$ in number (or less by reason of crystal symmetry) are accordingly monochromatic. In relation to the entire crystal, they are highly degenerate. The three missing degrees of freedom are exactly accounted for when the possible elastic vibrations which give a quasi-continuous spectrum of frequencies are enumerated. The limiting elastic wave-lengths come out as four times the lattice spacings of the crystal. The effects of anharmonicity are also considered. It is shown that they result in lowering and spreading out the spectral frequencies of the crystal when its temperature is elevated.

References

1. Blackman, M. .. *Proc. Roy. Soc.*, A, 1935, **148**, 390.
2. Born, Max .. *Atomtheories Das Festen Zustandes, Teubner*, Leipzig, 1923, 590.
3. Debye, P. .. *Ann. d. Phys.*, 1912, **39**, 789.
4. Herzberg, G. .. "Infra-Red and Raman Spectra of Polyatomic Molecules," *Von Nostrand*, 1945, Chapter II, Section 5.
5. Kellermann, E. W. .. *Phil. Trans. Roy. Soc.*, A, 1940, **238**, 513.
6. Raman, C. V. .. *Proc. Ind. Acad. Sci.*, A, 1943, **18**, 237.

THE VIBRATION SPECTRA OF CRYSTALS

Part II. The Case of Diamond

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CONTENTS

1. Introduction. 2. The Eigenvibrations. 3. The Valence Forces. 4. Numerical Evaluation of the Eigenfrequencies. 5. Activity in Light-Scattering. 6. Activity in Infra-Red Absorption. 7. The Spectroscopic Facts. 8. Summary.

1. Introduction

Of recent years, there has been a great accession of exact knowledge regarding the spectroscopic behaviour of crystals. Much of this knowledge has been gained by the method of investigation introduced by the present writer in the year 1928, namely, the spectral examination of the scattered radiations from crystals illuminated by monochromatic light. Valuable information has also come to hand from the study of luminescence spectra and of absorption spectra in the visible and ultra-violet regions at low temperatures. Considerable progress has also been made in the study of infra-red absorption by crystals. By working with thin films, and also by using the highest possible resolving powers, the inherent difficulties and imperfections of infra-red spectroscopy as applied to solids have been minimised. Critical investigations by these diverse methods concur in showing that the vibration spectrum of a crystal held at a sufficiently low temperature as observed in the infra-red region of frequency is effectively *a line spectrum*. From the fact that several procedures of experimental study which are wholly different in principle agree in their indications, it is clear that the spectra of crystals are inherently of this nature and not by virtue of any particular method of observing them.

The earlier theories of the subject which were based on ideas derived from the behaviour of elastic solids identified the atomic vibrations in a crystal with an immense number of " waves " of diverse wave-lengths and frequencies assumed to be present in it. This hypothesis led to a conception of the nature of the vibration spectrum of a crystal radically different from that stated above, *viz.*, that it is *a continuous spectrum*, both in the acoustic

and in the infra-red ranges of frequency. That such a view gained currency was perhaps not surprising at a time when experimental knowledge of the spectroscopic behaviour of crystals was of a meagre description. It is, however, altogether inconsistent with the facts known at present as the result of recent research, as will be shown in this paper and the others following it.

The case of diamond which we shall proceed to consider in detail is by far the most suitable test for any theory of the spectroscopic behaviour of crystals. For, it is the solid of the simplest structure and composition of which the vibration spectrum is amenable to theoretical calculation as well as to experimental study. Indeed, all the possible different methods of spectroscopic investigation—five in number—which can be applied to the study of a crystal have been successfully employed in the case of diamond. A further special advantage presented by diamond is that its vibration spectrum appears spread out over a wide range of frequency. This makes it possible with only instruments of moderate power to ascertain and establish the true nature of its spectrum unambiguously, while with the aid of more powerful instruments, it is possible to discover and demonstrate the finest details of its spectral behaviour. A further and notable advantage which arises from the high frequencies of atomic vibration in diamond is that the secondary effects due to thermal agitation are unimportant in its case even at ordinary temperatures. Such effects are markedly present in the majority of crystals and disturb the intrinsic simplicity of their spectra.

2. The Eigenvibrations

As is well known, the structure of diamond may be described as consisting of two similar Bravais lattices of carbon atoms of the face-centred cubic type interpenetrating each other. Each atom in one of the lattices is linked to four atoms in the other lattice by valence bonds along the four trigonal axes of symmetry of the crystal. The atoms in the two lattices appear in distinct layers in the octahedral as well as in the cubic planes. In the former set of planes, they are alternately nearer and further apart, while in the cubic planes they are equidistant. This disposition of the layers is a consequence of the quadrivalence of the carbon atoms and is represented in Fig. 1, for the octahedral planes and in Fig. 2 for the cubic ones. A_1 and A_2 represent successive layers of carbon atoms belonging to one lattice, while B_1 and B_2 represent successive layers belonging to the other.

In Part I of this series of papers, we have already derived the nine possible eigenvibrations of diamond, and they may be readily visualised with the help of a model of its structure. Figs. 1 and 2 above are also helpful in this connection. The principal oscillation of the structure is the one in

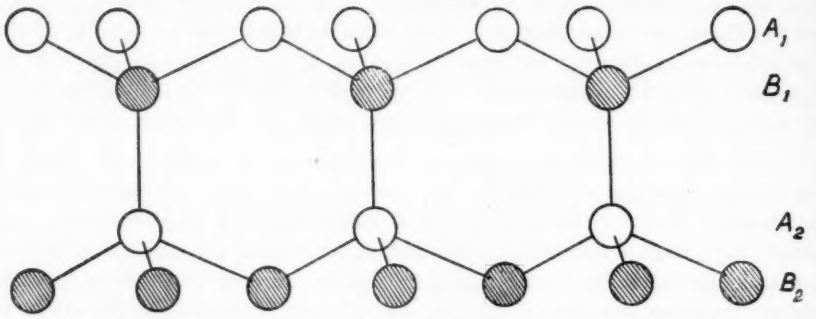

FIG. 1. Structure of Diamond viewed perpendicular to a trigonal axis

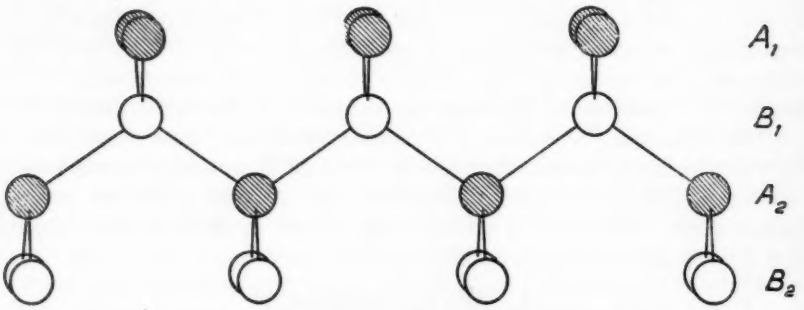

FIG. 2. Structure of Diamond viewed perpendicular to a cubic axis

which the atoms of each lattice move together in the same phase against the atoms in the other lattice moving together in the opposite phase. It is a triply degenerate oscillation, and hence the direction of motion may be either normal or tangential to the atomic planes in either of the two figures, *viz.*, up and down the printed page or horizontally across it. The other eight possible movements arise from the three pairs of possible alternatives; the oscillations may be of the octahedral or of the cubic planes of atoms; the oscillations may be normal or tangential to these planes; the oscillations may be symmetric or antisymmetric, adjacent layers of the structure belonging to the two lattices moving in the same phase in the symmetric modes, and in opposite phases in the antisymmetric ones. Thus, for instance, in the tangential symmetric oscillation of the octahedral planes, the layers A_1 and B_1 in Fig. 1 move together horizontally across the page against the layers A_2 and B_2 moving together in the opposite direction. Similarly, in the tangential antisymmetric oscillation of the cubic planes, the layers A_1 and

B_2 in Fg. 2 move together horizontally across the page against the layers B_1 and A_2 moving together in the opposite direction.

TABLE I

Descending order of Frequency	Degeneracy	Description of Mode
I ..	3	Oscillation of the two lattices
II ..	8	Tangential antisymmetric oscillation of the octahedral planes
III ..	6	Tangential symmetric oscillation of the cubic planes
IV ..	4	Normal symmetric oscillation of the octahedral planes
V* ..	3	Normal antisymmetric oscillation of the cubic planes*
VI* ..	3	Normal symmetric oscillation of the cubic planes*
VII ..	4	Normal antisymmetric oscillation of the octahedral planes
VIII ..	6	Tangential antisymmetric oscillation of the cubic planes
IX ..	8	Tangential symmetric oscillation of the octahedral planes

* *Note.*—Modes V and VI have the same frequency.

3. THE VALENCE FORCES

The forces coming into play when the atoms in diamond oscillate are principally of two kinds, *viz.*, those due to changes of bond-lengths and those due to changes of bond-angles. The forces of the first kind are predominantly of greater strength, and this fact taken together with the geometry of the modes enables us readily to arrange them in a descending sequence of frequency as shown in Table I. We shall, to begin with, consider only the forces due to the changes of bond-lengths. It is immediately evident that they are absent in the tangential symmetric oscillation of the octahedral planes, as also in the tangential antisymmetric oscillation of the cubic planes described in the preceding paragraph. These two modes have therefore the lowest frequencies and are accordingly placed at the bottom of the table. On the other hand, the tangential antisymmetric oscillation of the octahedral planes, and the tangential symmetric oscillation of the cubic planes both involve large variations of bond-length. By reference to Figs. 1 and 2, it is seen that the changes of bond-length in each case are exactly the same as in the analogous movements of the two lattices against each other in mode I. Accordingly, these three modes have the highest frequency and are placed at the top of the table. The four modes in which the atomic layers move normally to themselves remain to be considered. It is readily seen that the symmetric and antisymmetric normal vibrations of the cubic planes would

have identical frequencies owing to the disposition of the valence bonds and of the atoms in equidistant layers. On the other hand, the symmetric and antisymmetric normal oscillations of the octahedral planes are obviously different. A simple calculation based on the inclination of the valence bonds to the direction of movement shows that the symmetric oscillation would have a higher frequency than the antisymmetrical, while the normal oscillation of the cubic planes would have an intermediate frequency.

In the final ordering of the modes, we have also to consider the forces due to the variations of the bond-angles. These differ notably in the modes VIII and IX in which bond-length variations are totally absent, as also in the modes I, II and III in which they are of equal magnitude, and hence enable us to arrange them in the proper sequence of frequency. The tangential symmetric oscillation of the octahedral planes (mode IX) obviously involves variations of fewer bond-angles than the tangential antisymmetric oscillation of the cubic planes (mode VIII). It therefore now appears at the bottom of the table, with the latter immediately above it. The principal lattice oscillation (mode I) involves variations of all six bond-angles and is therefore placed at the top of the table, followed in order by the tangential antisymmetric oscillation of the octahedral planes (mode II) and the tangential symmetric oscillation of cubic planes (mode III) in which only three bond-angles and one bond-angle respectively vary sensibly. The nine eigenvibrations as thus finally arranged are shown in Table I.

4. Numerical Evaluation of the Eigenfrequencies

The descending sequence of frequency shown in Table I is sufficient to enable the modes of vibration manifesting themselves in the spectrum of diamond to be individually identified. It is possible, however, to go further and make a numerical estimate of the frequency of each of the modes, thereby confirming the assignment of the observed spectral frequencies to the different modes and placing their identification on a secure basis. We shall proceed to show how this may be done.

In any eigenvibration, equivalent atoms have the same amplitude of motion, and since the masses of the two sets of equivalent atoms in diamond are the same, it follows that the atomic displacements are also the same. It is sufficient therefore to find the forces acting on any one atom in a given mode of vibration to ascertain its frequency. The principal forces acting on each atom are (1) the force proportional to its own displacement, and (2) the forces proportional to the displacements of the four atoms with which it is linked by valence bonds. The displacements of the more distant neighbours would also give rise to forces, but these would be smaller, and owing

to the alternation of phase in successive layers would tend to cancel each other out. We may accordingly limit ourselves to the forces specified above.

We denote the three force-constants with which we are concerned by P, Q and R. P is the restoring force on the atom under consideration arising from a unit displacement of itself along a cubic axis. Q and R are the forces on the atom arising from a similar displacement of one of the atoms linked with it, Q being parallel to the displacement, and R perpendicular to it. P being taken as a positive quantity, it is evident that Q would be negative and that P/4 would be the order of magnitude of its numerical value or rather an upper limit for the same. For, the restoring force P may be regarded as due to the displacement of an atom relatively to its four nearest neighbours, though the more distant atoms may also sensibly contribute. Further, owing to the tetrahedral disposition of the valence bonds, R and Q would be nearly equal to each other. More definitely, it can be said that $Q > R > Q/2$. The upper limit Q for R would be reached if the forces arise solely from the variation of bond-length, but we know that this is not the case and that the variation of bond-angles has also to be considered. The lower limit for R, namely Q/2, is set by the consideration that the forces due to variation of bond-angles would then be so large that modes IV, V, VI and VII in Table I would no longer form a descending sequence of frequency. The ratios P: Q: R are thus known *a priori*, at least approximately, from considerations based on the structure of diamond.

TABLE II

Calculated and Observed Eigenfrequencies of Diamond

Mode	F (Operative Force-constant)	Q=−P/4 R=2Q/3	Q=−P/5 R=2Q/3	Q=−P/6 R=2Q/3	Observed Frequency
		cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
I ..	P−4Q	1332	1332	1332	1332
II ..	P−2Q−2R	1276	1282	1287	1250
III ..	P−4R	1216	1230	1240	1232
IV ..	P+2Q−4R	1018	1057	1087	1149
V & VI ..	P	942	993	1031	1088
VII ..	P−2Q+4R	860	925	973	1008
VIII ..	P+4R	544	678	770	752
IX ..	P+2Q+2R	385	573	688	620
	P=	6·28	6·975	7·536	×10^5 dynes per cm.
	Q=	−1·57	−1·395	−1·256	do
	R=	−1·047	−0·93	−0·837	do

Denoting the mass of the carbon atom by m, the frequency in wave-numbers by ν and the velocity of light by c, we write

$$4\pi^2\nu^2c^2m = F, \qquad (1)$$

where F is the operative force-constant, *viz.*, the magnitude of the force acting on the atom per unit displacement. This is shown for each of the different modes in the second column of Table II. The formulæ are readily derived by reference to the modes as described in Table I. We remark that P necessarily appears in each case. Q appears with a factor equal to the number of linked atoms which move in the same phase as the atom under consideration, less the number moving in the opposite phase; the factor is -4, -2, 0, $+2$, 0, -2, 0 and $+2$ respectively for the modes as listed. The force-component R is perpendicular to a cubic axis and does not therefore appear in the frequency expressions for modes I, V and VI, the motion being along a cubic axis. In the remaining modes, the movement is along a body-diagonal or a face-diagonal of the cube, and R therefore appears in the formulæ with a multiplying factor equal to the number of atoms effective in each case. A check on the formulæ is obtained by putting $Q = -P/4$ and $Q = R$, when the frequency comes out as the same for the first three modes, as zero for the last two and as a descending sequence for those between.

Table II makes a comparison of the observed frequencies with those calculated on the basis of the P : Q : R ratios shown at the head of each column, the corresponding numerical values of P, Q and R which give the frequency of the first mode as 1332 cm.$^{-1}$ being shown below. It will be seen that there is good agreement between the figures appearing in the last two columns, thus supporting the identification of the modes with the observed spectral frequencies, as well as the theoretical approach on which the calculations are based. The agreement is, of course, not perfect, but this is only to be expected, since the forces have been ignored which arise from the more distant atoms. The fact that Q comes out as $-P/6$ and not as $-P/4$ is a clear indication that such forces are small, but are not negligible. This interpretation of the discrepancies between the figures shown in the last two columns of Table II is completely confirmed by an investigation of K. G. Ramanathan (1947) appearing elsewhere in these *Proceedings*. The dynamics of the problem has been very fully worked out by him, taking account of no fewer than 28 atoms in the equations of motion.

5. Activity in Light-Scattering

We shall now consider the activity of the various modes of vibration in light-scattering. Equivalent atoms in the structure have the same phase in mode I, while they are alternately in opposite phases in successive layers in the other modes. The changes of optical polarisability therefore add up for mode I, while they cancel out (*to a first approximation*) in the other modes. Mode I is therefore active in light-scattering, while the others are not.

TABLE III

Theoretical Activity of the Eigenvibrations

(For explanation see text)

Serial order	Frequency cm.$^{-1}$	Light Scattering		Infra-red Absorption	
		1st Order	2nd Order	1st Order*	2nd Order
I ..	1332	Active	Strong	Inactive	Inactive
II ..	1250	Inactive	Strong	Inactive	Very Weak
III ..	1232	Inactive	Very Strong	Inactive	Very Weak
IV ..	1149	Inactive	Strong	Inactive	Weak
V & VI ..	1088	Inactive	Weak	Inactive	Strong
VII ..	1008	Inactive	Very Weak	Inactive	Strong
VIII ..	752	Inactive	Inactive	Inactive	Inactive
IX ..	620	Inactive	Inactive	Inactive	Inactive

* *Note.*—The entries in the fifth column of the table assume that the electronic structure of diamond has octahedral symmetry. For a discussion of the infra-red activity of the first order arising when this is not the case, see Section 7 below.

In the second approximation, the non-linear dependence of the optical polarisability on the atomic displacements has to be considered. It is evident that if the *increase* in optical polarisability due to the approach of two atoms is different from the *decrease* due to their recession by an equal amount, the effects of the successive layers would not cancel out completely, leaving a residue which passes through a complete cycle of changes twice during each oscillation and has therefore twice its frequency. Superposition of two modes with different frequencies would, in addition, yield a residual effect with a summational frequency. In considering the magnitude of such effects, it is useful to regard the valence bonds themselves as the units which are optically polarisable. We represent each bond as having an ellipsoid of polarisability of its own. The tetrahedral grouping of the ellipsoids in the crystal secures its optical isotropy in the non-oscillating state. Alterations of bond-lengths during a vibration produce changes in the axial dimensions of the ellipsoids, while variations of bond-angle would alter their orientations. Only major changes could be expected to give observable second-order effects. Accordingly, we are justified in assuming that only changes of bond-length would give such effects. The strength of the effects would be determined principally by the absolute magnitude of the variations of bond-length, and only to a lesser extent by the number of bonds so varying.

The activity of the various eigenvibrations has been assessed and shown in the fourth column of Table III on the basis of the foregoing considerations.

Modes VIII and IX do not involve changes of bond-length and should therefore be inactive. Mode VII is a normal oscillation of the octahedral layers involving changes of three bond-lengths out of every four, but these changes are very small. Accordingly, this mode should exhibit only a very weak second-order activity. Modes V and VI are normal oscillations of the cubic planes in which two out of every four bonds vary in length, but the changes are definitely larger than in mode VII. Their activity should therefore be greater than that of mode VII. In mode IV, only one bond out of every four varies, but the entire motion is along this bond, and the change in its length is therefore considerable. Accordingly, this mode should be strongly active. In the three remaining modes of highest frequency in the table, the bond-length variations are large, but the number of bonds varying is different, being four in mode I, three in mode II, and two in mode III. The *individual* variations in bond-length are greatest in mode III, less in mode II and least in mode I. Accordingly the second-order activity in light-scattering should be strongest in mode III, less in mode II, and least in mode I, though very considerable in all three cases.

The second-order activity is essentially dependent on the absolute magnitude of the atomic displacements and unless these are large, their results would be of negligible intensity. The atomic displacements are determined by the consideration that the energy of vibration is $h\nu$ for a single excitation and $2h\nu$ for a double excitation. The amplitudes of vibration would be very small and the second-order effects, therefore wholly unobservable if this energy be distributed over the entire volume of the crystal or even over a large number of lattice cells. We may remark further, that since the *elastic vibrations* of a crystal extend over its whole volume, they cannot exhibit any second-order activity in light-scattering. The first order activity is also cancelled out completely by optical interference except in the very special case of a coherent reflection.

6. Activity in Infra-Red Absorption

To simplify the discussion of the activity of the modes in infra-red absorption, we shall here restrict ourselves to the case in which the electronic structure of diamond can be assumed to possess octahedral symmetry. The distribution of electron density has then a centre of symmetry at the point midway between every pair of linked carbon atoms. Since, further, the carbon atoms have equal masses, these points would continue to be centres of symmetry of the electron distribution in mode I, which would therefore be inactive to all orders of approximation. The remaining modes (II to IX) would also be inactive but for a different reason, *viz.*, that the phase of

the vibration is reversed at each successive layer of atoms and the effects of successive layers would therefore cancel each other out in *the first approximation.*

We have now to consider whether the oscillations of the atomic layers in the modes II to IX would give rise to electric moments in the individual layers large enough to give an *observable second-order effect of double frequency.* The tetrahedral symmetry of diamond ensures that the atomic nuclei are also the centres of distribution of the negative electric charges surrounding them. But when the layers of atoms oscillate *normally* to themselves and the neighbours on either side of each layer do not move *symmetrically* with respect to it, the tetrahedral symmetry of distribution of charge would evidently be disturbed. As a result, each atomic plane would become an oscillating electric double layer, thereby giving rise to an observable second-order infra-red activity. A *tangential* oscillation of the atomic layers would, however, not be effective in the same manner or to the same extent. If, further, as in modes VIII and IX, the valence bonds only tilt but do not stretch, no appreciable dipole moments could develop. The relative activities of the various modes can be assessed on the basis of these considerations and are shown in the last column of Table III. We may remark that modes V and VI are normal oscillations of the cubic planes, while modes IV and VII are those of the octahedral planes. In mode VII, the closely adjacent atomic layers approach and recede from each other, while the more distant ones remain at the same distance. In mode IV, the situation is reversed, *viz.*, the closely adjacent layers remain at the same distance apart from each other, while the more distant one recedes and approaches. In these circumstances, it is clear that mode VII should exhibit greater infra-red activity than mode IV, as shown in the table.

7. The Spectroscopic Facts

The spectroscopic behaviour of diamond has been very thoroughly investigated at Bangalore with the result that we have a wealth of experimental results at our disposal. The data for the spectral frequencies obtained by different methods have been set together in parallel columns and represented in the form of a chart below (Fig. 3). For lack of space, the chart omits reference to the infra-red *emission* spectra. These, however, closely follow the corresponding *absorption* spectra.

The Scattering of Light.—Spectroscopic studies made prior to 1943 had revealed that diamond exhibits in light-scattering a frequency shift of 1332 $cm.^{-1}$, evidently representing our mode I. Following on the publication of his theory (Raman, 1943), the present writer confidently ventured to

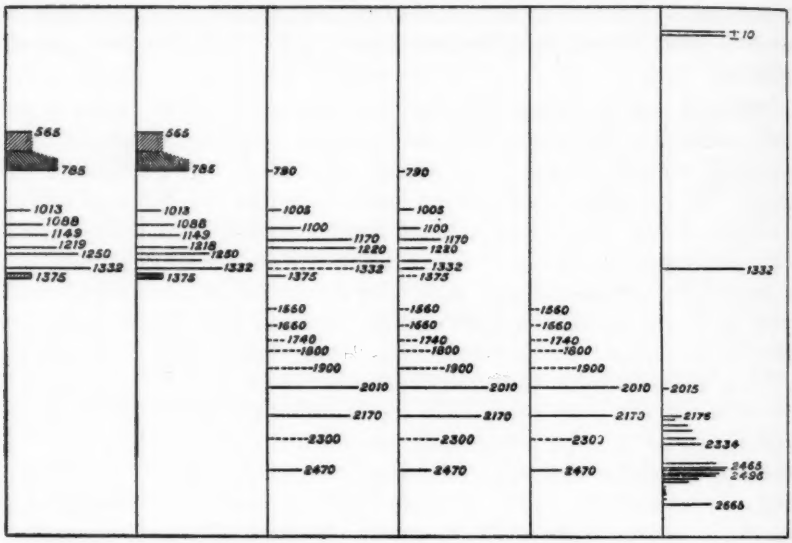

FIG. 3. Spectral Frequencies in cm.$^{-1}$ as observed by various methods

predict that diamond should also exhibit a second-order spectrum with other frequency shifts explicable as octaves and combinations of its eight fundamental frequencies. An experimental investigation undertaken by Dr. R. S. Krishnan soon afterwards confirmed this prediction. A detailed report on his latest findings appears in a paper by Dr. R. S. Krishnan (1947) appearing in these *Proceedings*. His earlier papers (1944, 1946) on the subject also contain valuable experimental material to which the reader is referred. It will suffice here to remark that these publications clearly establish the discrete character of the vibration spectrum of diamond indicated by the present theory. *Of particular significance is the notable intensity of the second-order spectrum in relation to that of the first order, which clearly demonstrates that the energy of the high-frequency vibrations in the crystal is not diffused through it in the form of a "wave", but is concentrated in extremely small regions comparable in volume with its lattice cells.* The interesting fact that the octave of the 1332 line is not the most intense one in the second-order spectrum,—being, in fact, the third in order of intensity—finds its explanation in the theoretical considerations set out in Section 5 of the present paper. Dr. R. S. Krishnan's earlier spectrograms did not reveal the octave of mode VII. The theoretical prediction that it should appear in the second-order spectrum though only with a very small intensity has, however, been confirmed in his most recent investigations.

Infra-Red Absorption.—All diamonds without exception exhibit an infra-red absorption in the region of frequencies between 1560 cm.$^{-1}$ and 2470 cm.$^{-1}$, the strength of which shows no appreciable variation from specimen to specimen. It is therefore clearly a fundamental property of diamond. The existence of such absorption and its spectral characters are explained by the theoretical considerations set out in Section 6 of the present paper. The two prominent peaks in infra-red absorption appearing at 2010 cm.$^{-1}$ and 2170 cm.$^{-1}$ are clearly the octaves of the fundamental frequencies 1008 and 1088.

A study of the crystal forms of diamond from a new point of view (Raman and Ramaseshan, 1946) has shown clearly that the crystal symmetry of diamond is, in general, only tetrahedral, though some diamonds undoubtedly possess the higher or octahedral symmetry of structure. The fact that the great majority of diamonds exhibit infra-red activity of the first order ceases to be surprising in the light of this finding. The striking variations in the strength of such activity in different specimens also find their natural explanation in the interpenetration of the positive and negative tetrahedral structures which is also clearly indicated by the crystallographic evidence. From our present point of view, these facts are chiefly interesting since infra-red activity of the first-order makes the fundamental frequencies themselves accessible to observation. The three columns marked (I), (II), (III) in Fig. 3 represent results typical of those observed with different diamonds.

A full report on the infra-red absorption spectra of numerous diamonds is made by K. G. Ramanathan (1947) in a paper appearing in these *Proceedings*. It will suffice here to make a few remarks supplementing those contained in Section 6 of the present paper on the theoretical aspects of the subject. The small difference in structure which gives rise to the first-order activity in most diamonds would not make any difference in respect of the second-order activity. Hence no changes are necessary in respect of the entries in the last column of our Table III. If there were no interactions between the different normal modes, tetrahedral symmetry would result in making mode I active, the other modes remaining inactive in the first approximation. Actually, however, the differences between mode I and the other modes are due only to the differences in the phases of movement of the atomic layers. In view of this geometric similarity of the movements and the anharmonicity of the forces arising from the atomic displacements, a strong interaction between the different " normal " vibrations is inevitable. Such interaction would be the more powerful, the smaller the difference of frequency between mode I and the other mode under consideration. We need not therefore be surprised to find, as is actually the case, that the infra-red

activity of mode I results in the modes with frequencies not very remote from it also showing an observable activity of the first-order.

Emission and Absorption by Luminescent Diamonds.—The emission spectra of luminescent diamonds are of two different kinds, *viz.*, "blue luminescence" and "yellow luminescence", and there are also two corresponding types of absorption spectra. These have their origin in electronic transitions which appear at λ 4152 and λ 5032 respectively and combine with vibrational transitions in the crystal, giving a spectrum stretching respectively towards longer wave-lengths in emission and towards shorter wave-lengths in absorption. The spectra are best studied with the diamond held at liquid air temperatures, the features observed in the spectra being then most sharply defined. The vibrational frequencies as determined from the emission and absorption spectra are practically identical. Indeed, these spectra exhibit a remarkable mirror-image symmetry about the electronic transition (λ 4152 or λ 5032 as the case may be), in respect of both position and distribution of intensity, thereby affording a clear demonstration that they arise from the combination of the electronic and vibrational frequencies of the crystal.

The spectroscopic behaviour of no fewer than 28 diamonds in luminescence and absorption has been investigated in detail by Miss Anna Mani (1944). Her paper may be consulted for a full report on the subject including further details. One of her most interesting findings is that the vibration spectra accompanying the λ 4152 and λ 5032 electronic transitions are strikingly different in respect of the distribution of intensity. The vibrational transitions accompanying the λ 4152 transition are principally those lying in the upper or infra-red range of frequency and their overtones, while those accompanying the λ 5032 electronic transitions are principally the "elastic" vibrations of lower frequency. Hence, the "blue" luminescence and corresponding absorption spectra are those which are important from our present point of view. Miss Mani has shown that the λ 4152 transition is really a doublet, the width of the components as well as their separation varying with the specimen under study. Even at liquid air temperature, the total width covered by the electronic transition is never less than 20 $cm.^{-1}$ and may be as such as 50 $cm.^{-1}$. This width necessarily appears in the spectra when the electronic frequency combines with the vibrational frequencies and hence obscures to some extent the monochromatic character of the latter. Even so, the discrete nature of the vibrational spectrum in the upper ranges of frequency is clearly manifest in the emission and absorption by "blue" luminescent diamonds when held at liquid air temperatures. The observed frequency differences are shown in our chart (Fig. 3).

8. Summary

Considerations based on the crystal structure of diamond enable its nine eigenvibrations to be arranged on a descending scale of frequency. The magnitude of the force-constants involved can also be defined within narrow limits. The numerical values of the frequencies evaluated on the basis of the theoretical formulæ show a close agreement with the observed values. The geometry of the modes determines the changes in bond-polarisabilities and electron distributions produced by them, from which their activities in light-scattering and in infra-red absorption can be ascertained both in the first and in the second approximation. A comparison of the results with the experimental facts shows a striking agreement. The observed intensity of the second-order effects in relation to those of the first order indicates that the eigenvibrations are localised in volume elements comparable in size with the lattice cells of the crystal.

References

Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, **A**, 1947, **26**.
——— .. *Ibid.*, 1944, **19**, 216.
——— .. *Ibid.*, 1944, **19**, 298.
——— .. *Ibid.*, 1946, **24**, 25.
——— .. *Ibid.*, 1946, **24**, 45.
Mani, Miss Anna .. *Ibid.*, 1944, **19**, 231.
Raman, C. V. .. *Ibid.*, 1943, **18**, 237.
——— and Ramaseshan, S. .. *Ibid.*, 1946, **24**, 1.
Ramanathan, K. G. .. *Ibid.*, 1947, **26**, 481.
——— .. *Ibid.*, 1947, **26**, 469.

THE VIBRATION SPECTRA OF CRYSTALS

Part III. Rocksalt

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CONTENTS

1. Introduction. 2. The Nature of the Interatomic Forces. 3. The Eigenvibrations. 4. Evaluation of the Eigenfrequencies. 5. Activity in Light Scattering. 6. Activity in Infra-Red Absorption. 6. The Spectroscopic Facts. 7. Summary.

1. Introduction

Rocksalt is typical of the so-called ionic crystals and is a much-discussed substance. The evaluation of its characteristic vibration frequencies on the basis of the theory set out in Part I, and the consideration of its spectroscopic behaviour in the light of that theory will form the subject of the present paper. From an experimental point of view, the case of rocksalt is a less favourable one than that of diamond, the frequencies being very low and hence crowded together into a region of the spectrum where observation is difficult and the available resolving powers are small. Nevertheless, as we shall see, the main facts have been quite clearly established and are in striking accord with the theoretical deductions.

2. Nature of the Interatomic Forces

Discussions of the energy of formation of the alkali halides and of their physical properties usually proceed on the basis that the main interaction between the constituent particles in these crystals is the ordinary electrostatic or the Coulomb force between the ions, and that these forces which tend to contract the dimensions of the crystal are balanced by repulsive forces which vary much more rapidly with interatomic distance than do Coulomb forces between charges. Various additional interactions, *e.g.*, Van der Waals forces, have also been considered by way of refinement of the theory. That the electrostatic or the Madelung term is the largest in the expression for the cohesive energy of the alkali halides thus derived might lead one to believe that the electrostatic forces would also principally determine the frequencies of vibration of the ions about their positions of equilibrium. Actually, however, this is not the case, as may readily be shown by considering the consequencies of the cubic symmetry of the ordering of the ions in the crystal.

Since the electrostatic forces acting on the ions vanish when they are located at the points of the lattice, it follows that at these points $(\partial V/\partial x) = (\partial V/\partial y) = (\partial V/\partial y) = 0$, where V represents the electrostatic potential in the vicinity of a lattice point due to all the ions except the one which is situated at that point. The cubic symmetry of the ordering also demands that $(\partial^2 V/\partial x^2) = (\partial^2 V/\partial y^2) = (\partial^2 V/\partial z^2)$. Combining these relations with Laplace's theorem which states that the sum of these three quantities is zero, it follows that each of them would be individually zero. In other words, not only does the electrostatic field at a lattice point due to the surrounding ions vanish, but it also vanishes in its immediate vicinity. If, therefore, one of the ions is displaced a little from its position of equilibrium, the surrounding ions being undisturbed, there would be no force tending to restore the displaced ion to its position of equilibrium. The same situation would arise if we imagine all the Na^+ ions to be displaced a little in one direction and all the Cl^- ions to be displaced a little in the opposite direction, so that each set of ions retains its cubic symmetry of arrangement. The resultant electrostatic force on each Na^+ ion and on each Cl^- ion in their displaced positions would vanish, and the frequency of the resulting oscillation would be zero, if forces of other descriptions were non-existent. We are accordingly compelled to recognize that the frequency of the vibration would be determined entirely by interatomic forces which are not primarily of electrostatic origin. It follows that these are essentially short-range forces which have a considerable magnitude as between neighbouring atoms but diminish very quickly as between more distant ones.

3. The Eigenvibrations

As in the case of diamond discussed in the preceding paper, the rocksalt structure has nine eigenvibrations, eight of which may be described as normal or tangential oscillations of the octahedral or cubic layers of ions *alternately in opposite phases*, and the ninth as an oscillation with respect to each other of the two interpenetrating lattices of Na^+ and Cl^- ions respectively. These modes may be readily visualised with the aid of diagram of the structure of rocksalt (Fig. 1). As in the case of diamond again, the first step we shall take is to arrange these nine eigenvibrations in a descending sequence of frequency, thereby facilitating a comparison of the theoretically derived spectrum with the experimental data. Such arrangement is readily possible in view of the conclusion stated earlier, *viz.*, that the atomic interactions which determine the vibration frequencies are short-range forces.

We may, in the first instance, consider the interactions between each Na^+ ion and the 6 surrounding Cl^- ions and similarly also the interaction

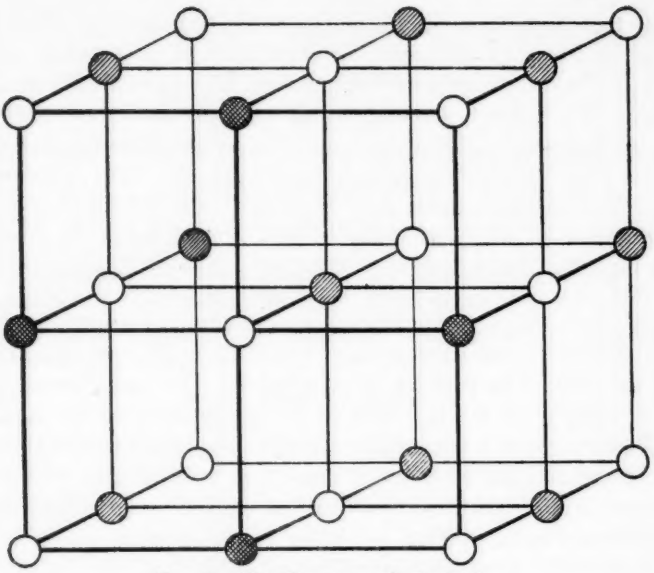

FIG. 1. The Structure of Rocksalt

between each Cl^- ion and the six surrounding Na^+ ions, *neglecting the forces due to the more distant ions in each case*. So long as the octahedral grouping of the surrounding ions is undisturbed, the restoring force per unit displacement acting on the central ion when it is displaced would be independent of direction, and it is also evident that it would be the same whether it is Na^+ or Cl^-. We shall denote this force by P and assume that it arises from an approach or recession of the Na^+ and Cl^- ions relatively to each other. The frequency of an oscillation would accordingly be determined by the magnitude of such displacements and by the masses of the moving particles. On this basis, the nine eigenvibrations fall into four groups, consisting of 3, 2, 2 and 2 respectively, each group having the same frequency. The first group of 3 eigenvibrations consists of:

(I) The *normal* oscillation of the cubic planes with Na^+ and Cl^- ions in these planes moving *in the same phase*;

(II) the *tangential* oscillation of the cubic planes, with the Na^+ and Cl^- ions in these planes moving in *opposite phases*; and

(III) the oscillation of the Na^+ and Cl^- lattices against each other *in any arbitrary direction.*

It can be seen from Fig. 1 that the displacements of the Na^+ and Cl^- ions relatively to each other are the same in all these three cases. Accord-

ingly, the operative force-constant is equal to P and the frequency ν of vibration in wave-numbers is given by the formula

$$4\pi^2\nu^2c^2 = P\left(\frac{1}{m_1} + \frac{1}{m_2}\right) \tag{1}$$

m_1 and m_2 being the masses of the Na^+ and Cl^- ions respectively. The second group of eigenvibrations consists of

(IV) the normal oscillations of the Na^+ ions in the octahedral planes, the Cl^- ions remaining at rest; and

(V) the tangential oscillations of the Na^+ ions in the octahedral planes, the Cl^- ions remaining at rest. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = P \cdot \frac{1}{m_1} \tag{2}$$

The third group of eigenvibrations consists of

(VI) the normal oscillations of the Cl^- ions in the octahedral planes, the Na^+ ions remaining at rest: and

(VII) the tangential oscillations of the Cl^- ions in the octahedral planes, the Na^+ ions remaining at rest. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = P \cdot \frac{1}{m_2}. \tag{3}$$

The fourth group of eigenvibrations consists of

(VIII) the normal oscillations of the cubic planes of atoms, the Na^+ and Cl^- ions in these planes moving *in opposite phases* and

(IX) the tangential oscillations of the cubic planes of atoms, the Na^+ and Cl^- ions in these planes moving *in the same phases*. These two oscillations have the frequency

$$4\pi^2\nu^2c^2 = 0. \tag{4}$$

For a final ordering of the nine eigenvibrations in a descending sequence of frequency, we have to consider also the forces of interaction between each Na^+ ions and the 12 surrounding Na^+ ions, and similarly also the forces between each Cl^- ion and the 12 surrounding Cl^- ions. It is readily seen that mode I would then have the highest frequency in the first group, since 8 out of the 12 like ions move in the opposite direction to the ion under consideration and thereby increase the restoring force. In mode II, 4 of the like ions move in the same direction and 4 in the opposite direction, cancelling out each other's effects. In mode III, all the 8 like ions which exert appreciable forces move in the same direction, thus diminishing the restoring force and therefore also the vibration frequency. The 3 modes thus arrange themselves in the order indicated. In the second and third groups it is readily seen from considerations similar to those stated

above, that the normal modes would have higher frequencies than the tangential ones. This is also the case in the fourth group, the frequencies of which no longer vanish when the forces between like ions are taken into consideration. These have naturally the lowest frequencies of all the nine eigenvibrations. Table I summarises the foregoing results.

TABLE I

Eigenvibrations of the Rocksalt Structure

Descending sequence of frequency	Degeneracy	Oscillating units	Direction of motion	Detailed description
I ..	3	Cubic Planes	Normal	Na and Cl ions moving in the same phase
II ..	6	Cubic Planes	Tangential	Na and Cl ions moving in opposite phases
III ..	3	Two lattices	Arbitrary	Na and Cl ions moving in opposite phases
IV ..	4	Octahedral Planes	Normal	Na ions moving and Cl ions at rest
V ..	8	Octahedral Planes	Tangential	Na ions moving and Cl ions at rest
VI ..	4	Octahedral Planes	Normal	Cl ions moving and Na ions at rest
VII ..	8	Octahedral Planes	Tangential	Cl ions movings and Na ions at rest
VIII ..	3	Cubic Planes	Normal	Na and Cl ions in opposite phases
IX ..	6	Cubic Planes	Tangential	Na and Cl ions in same phases

4. EVALUATION OF THE EIGENFREQUENCIES

To carry the matter a step further and evaluate the frequencies of each of the nine eigenvibrations, we shall make use of the exact theoretical formulæ derived by K. G. Ramanathan (1947) in a paper appearing in these *Proceedings* which take into account the interaction between the ions of each kind and their 26 nearest neighbours. They contain 11 independent constants which express the forces arising from such interactions and are connected by two additional relations. Ramanathan's formulæ may be simplified by ignoring the effect of the 8 most remote ions expressed by his constant V appearing in them, and also by putting his constants R, S and S′ all equal to zero. The former step is justified on the view that we are here concerned with short-range forces, and the latter by the consideration that the constants R, S and S′ refer to forces which arise from displacements which do not alter the distance between the interacting ions. On any reasonable view of the origin of the interactions in an ionic crystal with cubic symmetry, such forces should be vanishingly small in comparison with the forces arising from displacements which alter the distances between the

interacting ions. It may be remarked also that T and U in Ramanathan's formulæ represent forces between two ions of the same kind arising from a unit displacement of one of them, the force T being parallel to the displacement and the force U transverse to it, both being inclined at the same angle of 45° to the line joining the two interacting ions. In these circumstances and considering the ionic nature of the structure, it is a justifiable simplification of the formulæ to put $T = U$ and similarly also $T' = U'$. With these simplifications, the final formulæ contain only four unknown constants P, P', T, T' which are connected by the relation

$$(P + 8T) = (P' + 8T') \tag{5}$$

Further,

$$P \gg T \text{ and } P' \gg T' \tag{6}$$

from which it follows

$$P \backsimeq P' \tag{7}$$

The formulæ for the frequency of the nine eigenvibrations as thus simplified are listed in Table II.

TABLE II

Frequency Expressions

P and P' are positive ; T and T' are negative.

Descending sequence of frequency	$4\pi^2\nu^2c^2$	Description of mode
I ..	$\frac{P-8T}{m_1} + \frac{P'-8T'}{m_2} + \frac{16(T+T')}{m_1+m_2}$	Normal oscillation of cubic planes with Na and Cl in same phase
II ..	$\frac{P}{m_1} + \frac{P'}{m_2} + \frac{8(T+T')}{m_1+m_2}$	Tangential oscillation of cubic planes with Na and Cl in opposite phases
III ..	$\frac{P+8T}{m_1} + \frac{P'+8T'}{m_2}$	Oscillation of the two lattices in opposite phases
IV ..	$\frac{P-8T}{m_1}$	Normal oscillation of Na ions in octahedral planes
V ..	$\frac{P+4T}{m_1}$	Tangential oscillation of Na ions in octahedral planes
VI ..	$\frac{P'-8T'}{m_2}$	Normal oscillation of Cl ions in octahedral planes
VII ..	$\frac{P'+4T'}{m_2}$	Tangential oscillation of Cl ions in octahedral planes
VIII ..	$-\frac{16(T+T')}{m_1+m_2}$	Normal oscillation of cubic planes with Na and Cl in opposite phases
IX ..	$-\frac{8(T+T')}{m_1+m_2}$	Tangential oscillation of cubic planes with Na and Cl in same phase

One of the noteworthy features which emerge from the table is that the vibration in which the two lattices move in opposite phases is not that of the highest frequency but is only the third in the list, though the frequency differences between it and the two others above are not large. The four modes appearing in the middle of the table fall into pairs whose frequencies are approximately as the square roots of the masses of the chlorine and the sodium ions. The two modes at the foot of the table stand out from the rest by reason of the fact that their frequencies depend only on the weak interactions between similar ions instead of on the stronger interactions between the dissimilar ones, as in the case of the other modes. It will be noticed that the ratio of their frequencies is $\sqrt{2}$.

5. Activity in Light-Scattering

The eight eigenvibrations which are movements of the cubic and octahedral layers of atoms in the crystal are necessarily inactive in light-scattering *in the first approximation*, since the motion is in opposite phases in alternate layers. The oscillation of the lattices of Na and Cl ions with respect to each other is also inactive but for a different reason, namely the location of the Na and Cl ions alternately along the cube axes, in consequence of which the variations of their optical polarisability resulting from their movements cancel out *in the first approximation.*

In the second approximation, all the nine modes may be active, giving rise to octaves and combinations of the fundamental frequencies as shifts in light-scattering. The intensity of the observable effects would however depend notably on various factors, including especially the nature of the movements of the neighbouring Na and Cl ions with respect to each other. These movements are very similar in modes I, II and III, the two Cl^- ions on each side of a Na^+ ion along the cube axis respectively approaching and receding from it, while the two Na^+ ions on each side of a Cl^- ion behave similarly with respect to the latter. *Provided the amplitude of atomic movements is sufficiently large*, which would be the case in the present theory which regards the movements as restricted to extremely small volume elements in the crystal, each pair of neighbouring Na^+ and Cl^- ions at the phase of their nearest approach would have a polarisability greater than the value averaged over the whole period, thus giving rise to a variation of double frequency. Modes I, II and III would therefore all be active to much the same extent, but since mode II has a degeneracy 6, it should appear as the octave more strongly than either mode I or III which has a degeneracy of 3 only.

We may now consider modes IV and V which represent oscillations of the Na^+ ions only lying in the octahedral layers, as also modes VI and VII

which represent similar oscillations of the Cl^- ions only. We notice that the nature of the approach of the Na^+ and Cl^- ions to each other is very different in the normal and tangential modes in each case. In the normal modes, *viz.*, IV and VI, six ions of one kind simultaneously approach or recede from an ion of the other kind, while in the tangential modes, *viz.*, V and VII, two ions of one kind approach, two recede, and two others remain at the same distance. Hence the changes of polarisability should be much larger in the normal modes IV and VI than in the tangential modes V and VII. Further, since the refractivity of the Cl^- ion is very much larger than that of Na^+, it follows that mode VI in which the six Cl^- ions surrounding a Na^+ ion simutaneously approach or recede from it should display a much stronger activity in light-scattering than mode IV in which six Na^+ ions simultaneously approach or recede from a Cl^- ion. Indeed, one may justifiably infer that in respect of intensity in second-order scattering, mode VI would transcend in intensity all the other eight modes. Mode VIII which is a normal oscillation of the cubic planes involves only small changes in the relative distance of the Na^+ and Cl^- ions and should therefore be very weak in light scattering, while mode IX which is a transverse oscillation of the same planes should be still weaker.

6. Activity in Infra-Red Absorption

Since the two interpenetrating lattices in the structure of rocksalt consist of dissimilar particles, their oscillation against each other (mode III in our table) is necessarily active in infra-red absorption. In all the other eight eigenvibrations, the phase of the motion is reversed at each successive layer, and hence *if regarded as independent normal vibrations of the structure*, they should be inactive in respect of infra-red absorption. The assumed independence of the modes in respect of their excitation by infalling radiation is, however, very far from corresponding with reality. Owing to the anharmonicity and the finite amplitudes of oscillation, the different eigenvibrations are in effect coupled with each other, and hence any one mode which is active would induce an activity in the other so-called inactive modes. Modes I and II are very similar to mode III in their general character, since the latter may be regarded as being either a normal or a tangential oscillation of the layers of the Na^+ and Cl^- ions in the crystal parallel to the cubic planes. They also differ from it comparatively little in frequency. Hence the intense activity of mode III, consequential on the Na^+ and Cl^- ions carrying opposite charges of electricity, must necessarily also result in inducing a strong activity of modes I and II. Mode III may likewise be regarded as a normal or tangential oscillation of the octahedral layers of the Na^+ and Cl^- ions in the crystal against each other. Hence the intense activity of mode

III would similarly induce an activity of modes IV, V, VI and VII, but in a much less measure than in the case of modes I and II, since the former involve only the Na^+ or the Cl^- layers moving but not both, and also since the approximation in frequency is much less close. We may therefore conclude that the first-order infra-red activity of rocksalt would be very strong for modes I, II and III, and would fall off rapidly as we pass successively to modes IV, V, VI and VII. Modes VIII and IX could scarcely be expected to show any such induced activity of the first order in view of their very low frequencies.

Second-order infra-red activity may arise either from mechanical or electrical anharmonicity. In the present case, since the Na^+ and Cl^- ions carry electric charges, it is the mechanical anharmonicity with which we are principally concerned. Since mode III has an intense first-order activity, it should also be active in the second order. The other eight modes being inactive in the first order if regarded as independent normal vibrations, they can be active in the second order only by reason of electrical anharmonicity. Such activity would however be much less important in the circumstances of the case than the activity induced by their proximity in frequency to the intensely active fundamental vibration, *viz.*, mode III. In other words, such of the octaves and combinations of the various primary frequencies as are not too remote from the fundamental frequency of mode III may be expected to become active to an extent determined principally by such contiguity.

7. The Spectroscopic Facts

The results set out in the four preceding sections taken as a whole give us a theoretical picture of the spectroscopic behaviour of rocksalt capable of being compared with the picture of the actual facts as observed by various investigators. Such a comparison shows a striking agreement, both generally and in details, and thus confirms the correctness of the theoretical approach made to the problem. For the sake of convenience, we shall make the comparison in three successive steps.

The Frequency Spectrum.—Table II gives the theoretical formulæ for the frequencies in terms of four force-constants, *viz.*, P, P′, T and T′. These constants are not all independent but are connected with each other by the relation $(P + 8T) = (P' + 8T')$, with the further indication that P and P′ are nearly equal to each other, and that both are very much larger than T and T′. We can make use of these relationships to simplify the formulæ still further by replacing both P and P′ in the expressions by a single constant P which is the mean of the two, and similarly replacing T and T′ by a single constant T which is their mean. From the structure of the formulæ, it is evident that such replacement would not materially alter the numerical

TABLE III

Calculated and Observed Values of the Eigenfrequencies

$P = 2.422 \times 10^4$ dynes per cm. $T = -0.053 \times 10^4$ dynes per cm.

Serial Order	$4\pi^2\nu^2c^2$	Calculated Frequency	Observed Frequency	Activity in Light-scattering
		cm.$^{-1}$	cm.$^{-1}$	
I ..	$\frac{P-8T}{\mu} + \frac{32T}{m_1+m_2}$	172	175	Strong
II ..	$\frac{P}{\mu} + \frac{16T}{m_1+m_2}$	164	167	Very Strong
III ..	$\frac{P+8T}{\mu}$	157	150	Strong
IV ..	$\frac{P-8T}{m_1}$	145	143	Strong
V ..	$\frac{P+4T}{m_1}$	128	129	Weak
VI ..	$\frac{P-8T}{m_2}$	117	117	Very Strong
VII ..	$\frac{P+4T}{m_2}$	103	101	Weak
VIII ..	$-\frac{32T}{m_1+m_2}$	70	67	Very Weak
IX ..	$-\frac{16T}{m_1+m_2}$	50	43	Very Weak

value of any of the frequencies, while on the other hand, it affords the advantage of enabling us to express all the nine frequencies in terms of two independent constants only, one of which is very much larger than the other. Table III shows the formulæ as thus simplified in the second column, μ being the usual symbol for the reduced mass of the Na^+ and Cl^- ions. With the assumed values of P and T shown at the head of the table, the numerical values have been calculated and shown in the third column in wavenumbers. The fourth column shows the observed frequencies, derived from the investigation by Dr. R. S. Krishnan on the second-order spectrum of light-scattering reported in these *Proceedings* (1947). It will be noticed that there is excellent agreement throughout.

Activity on Light-Scattering.—In his paper on the case of rocksalt appearing in these *Proceedings*, Dr. R. S. Krishnan (1947) has set out and discussed the facts ascertained by him in full detail, and it is scarcely necessary therefore to traverse the same ground here. It is sufficient to remark

that in all respects, *viz.*, the discrete structure of the spectrum, the magnitude of the frequency shifts and the relative intensities with which they appear, the experimental facts are in agreement with the indications of theory set out in Section 5 above. Of particular significance is the observation made by Krishnan that the sharp and intense line with a frequency shift of 235 cm.$^{-1}$, which is a conspicuous feature in the spectrum as recorded even with small instruments, remains sharp and gains in intensity relatively to the rest of the spectrum when recorded with instruments of higher dispersion and greater resolving power, thereby clearly demonstrating its monochromatic character. As will be seen from Table III, this line represents the octave of mode VI. It appears with an intensity transcending that of all other features in the spectrum, a fact which is readily understood since in this mode, the Cl^- ions which have a far higher refractivity than the Na^+ ions simultaneously approach towards or recede away from the latter in groups of six at a time.

Activity in Infra-Red Absorption.—The fundamental mode of highest frequency and its overtones sharply define the upper limits of frequency of the successive orders of spectra. Expressed in wave-lengths, these limits are respectively 57 μ, 29 μ, 19 μ and 14 μ. On our present theory, we should expect large changes in the behaviour of rocksalt on passing over these limits. In agreement with this expectation, the observational data show a transition from nearly perfect transparency to practically complete opacity for a thickness of 5 cm. in the wave-length range from 14 μ to 19 μ. A similar transition occurs for a thickness of 0·05 cm. in the wave-length range of 19 μ to 29 μ, and for a thickness of 0·0005 cm. in the wave-length range from 29 μ to 57 μ. For the last mentioned thickness the most intense absorption is found in the region from 57 μ to 66 μ which includes the frequencies of the three most strongly active modes I, II and III. The overall picture of the observed behaviour of rocksalt is thus in accord with the indications of the theory.

In view of the numerous overtones and combinations present and also considering the prominent role played by mechanical anharmonicity in the absorption of infra-red radiations by rocksalt, we would not be justified in expecting the absorption data to show up the discrete character of the vibration spectrum very obviously. Even if theoretical considerations had permitted any such result, the low resolving powers used and the difficulties of observation in the remote infra-red would prevent its realisation. Some indications of the discrete structure of the spectra are however forthcoming from the work of Czerny (1930) and Barnes and Czerny (1931). These authors have studied the variation with wave-length in the reflecting power of a rocksalt plate at nearly normal incidence, and also the variations of the transmission coefficient with wave-length for plates of different thicknesses.

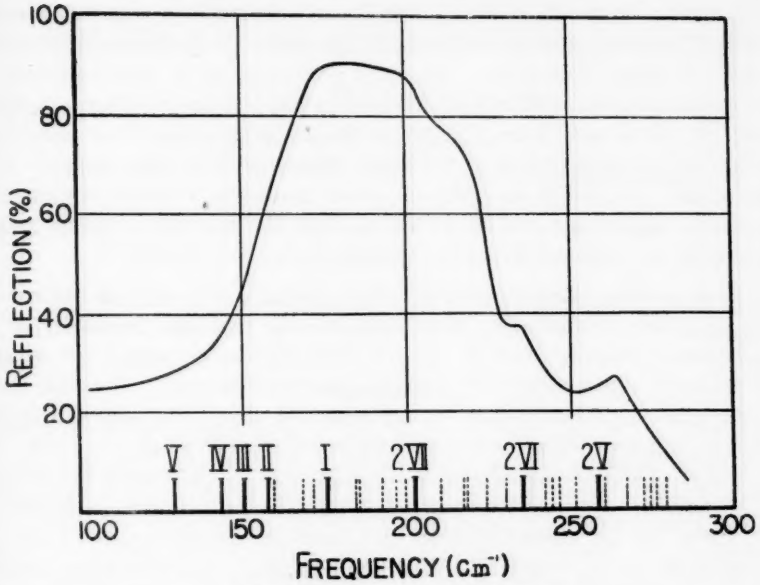

FIG 2. Reflecting Power of a Rocksalt Plate

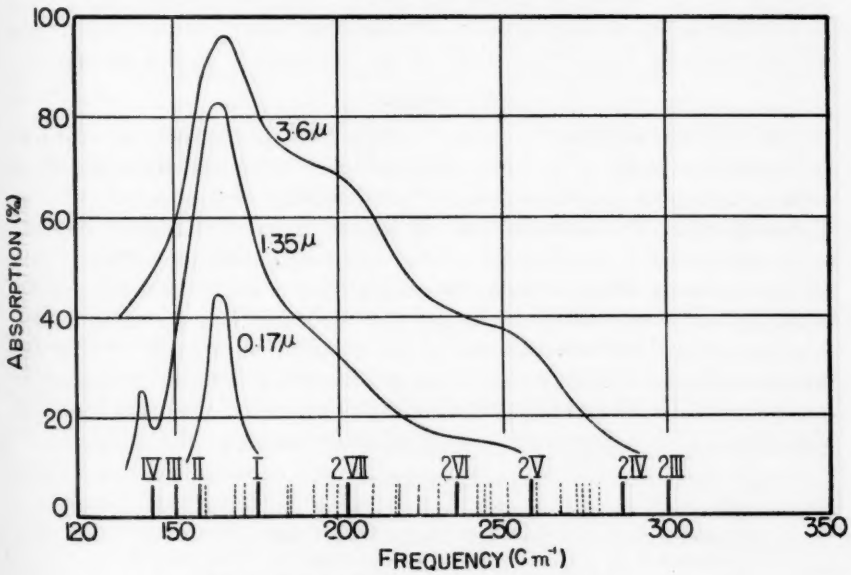

FIG. 3. Absorption Spectra of Rocksalt Films

Their results are shown in Figs. 2 and 3, carefully redrawn with wavenumbers instead of wave-lengths as abscissæ; for purposes of comparison, the fundamental vibration frequencies and their overtones have been indicated on the abscissæ by heavy lines and the various possible combinations by dotted lines. It will be seen from Fig. 2 that the reflecting power rises steeply and reaches its maximum value at the point where the first-order vibration spectrum ends. The fall of the reflecting power in the region of the second-order spectrum is less abrupt and shows undulations, the positions of which roughly agree with the overtone frequencies of our modes VII, VI and V.

It is a noteworthy feature in Fig. 3 that the "peak" of absorption even with the thinnest films does not coincide with the frequency of the oscillation of the Na^+ and Cl^- lattices with respect to each other which is our mode III, but is shifted definitely to a higher frequency. The explanation of this effect is evidently that besides mode III, there are other modes, *viz.*, I and II, and also various combinations in the vicinity which are active, and the course of the absorption curve is determined by the superposition of all their activities. The subsidiary maximum at 143 $cm.^{-1}$ noticed in the absorption curve for the second thinnest film may be identified with the fundamental frequency of mode IV. With the thickest of the three films, undulations are noticed in the absorption curve at approximately the same frequencies as the octaves of modes VII and V. Mentzel (1934) has recorded an inflexion in the absorption curve of rocksalt at about 290 $cm.^{-1}$ which may be interpreted as due to the activity of the overtones of modes III and IV.

7. Summary

It is pointed out that the vibration frequencies of the rocksalt structure are determined entirely by short-range atomic interactions, since the effects of the Coulomb forces cancel out. The numerical evaluation of the nine eigenfrequencies on this basis leads to results in excellent accord with the observational data. Their activities in light-scattering and infra-red absorption are also discussed. The vibration most strongly active in light-scattering is that of the Cl^- ions normal to the octahedral planes, the Na^+ ions remaining at rest. It is also pointed out that the peak of the infra-red absorption at 61 μ for thin films observed by Barnes and Czerny does *not* represent the frequency of oscillation of the Na and Cl lattices with respect to each other, but is shifted with respect to it owing to the activity of other modes in the vicinity.

References

Barnes and Czerny .. *Zeit. f. Physik*, 1931, **72**, 447–461.
Czerny .. *Ibid.*, 1930, **65**, 600.
Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, 1947, **26**, 419.
Mentzel .. *Zeit. f. Phys.*, 1934, **88**, 178.
Ramanathan, K. G. .. *Proc. Ind. Acad. Sci.*, 1947, **26**, 493.

THE VIBRATION SPECTRA OF CRYSTALS

Part IV. Magnesium Oxide

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CONTENTS

1. Introduction. 2. Evaluation of the Nine Fundamental Frequencies. 3. Their Infra-Red Activities. 4. Analysis of the Absorption Curves. 5. Summary.

1. Introduction

Magnesium oxide crystallises in the cubic system and X-ray diffraction studies show that its structure is similar to that of rocksalt. The high values of its density and elastic constants indicate, however, that the atomic interactions are far stronger in magnesium oxide than in rocksalt. This circumstance taken in conjunction with the low atomic weights of magnesium and oxygen has a notable influence on the vibration frequencies of the structure. Instead of being crowded together in the remote infra-red as in the case of rocksalt, the spectral frequencies are high and widely separated from each other and by the same token are very little influenced by thermal agitation. Magnesium oxide is accordingly a perfect choice for a material that would demonstrate by its spectral behaviour the monochromatic character of the atomic vibration frequencies in crystals. This indication of theory is strikingly borne out by the observations of Barnes and Brattain (1935) on its infra-red absorption spectrum. Employing plates of five widely different thicknesses obtained by cleavage from a large synthetically prepared single crystal, they recorded their absorption-curves with a rock-salt spectrometer, using an amplifying arrangement which gave a 150-fold magnification of the galvanometer deflections. The results showed the presence of some 40 well-defined absorption lines between 6μ and $15{\cdot}5\mu$, those of shorter wavelengths being most clearly exhibited by the thicker plates and those of longer wavelengths by the thinnest of the five plates.

In view of the similarity of structure, the nine fundamental frequencies of MgO may be evaluated with the aid of the same formulæ as in the case of rocksalt considered in the preceding paper. The three fundamentals with the highest frequencies are found to fall within the region investigated

by Barnes and Brattain, and their positions can be checked from the absorption curves published by these authors. The positions of the other six fundamentals as evaluated from the formulæ find exerimental support in the observations made by Strong (1931 *a*, *b*) and by Fock (1934) in the region of wavelengths beyond the reach of a rocksalt spectrometer. The numerous other absorption lines noticed by Barnes and Brattain are evidently the overtones and summations of the nine fundamental frequencies.

2. Evaluation of the Nine Fundamental Frequencies

Some idea of the magnitude of the forces which hold the magnesium and oxygen atoms together in the crystal may be obtained from the results of the analysis of the band spectra of MgO in the state of vapour (P. C. Mahanti, 1932). The vibration frequencies as deduced from the "red" and "green" systems of bands are respectively 822 cm.$^{-1}$ and 812 cm.$^{-1}$

Table I

Calculated Eigenfrequencies of Magnesium Oxide

$P = 2{\cdot}82 \times 10^5$ dynes per cm, $T = -0{\cdot}05 \times 10^5$ dynes per cm. m_H = mass of hydrogen atom.

Designation	Description of Mode	Degeneracy	$4\pi^2\nu^2c^2m_H$	Calculated Frequency	Calculated Wave-length
				cm.$^{-1}$	μ
ν_1	Normal oscillation of cubic planes, Mg and O atoms in same phase.	3	0·1037P − 0·036T	704	14·2
ν_2	Tangential oscillation of cubic planes, Mg and O atoms in opposite phases.	6	0·1037P + 0·397T	680	14·7
ν_3	Oscillation of Mg and O lattices in opposite phases.	3	0·1037P + 0·830T	652	15·35
ν_4	Normal oscillation of octahedral layers of O atoms, Mg being at rest.	4	0·0625P − 0·5T	584	17·1
ν_5	Tangential oscillation of octahedral layers of O atoms, Mg being at rest.	8	0·0625P + 0·25T	527	19·0
ν_6	Normal oscillation of octahedral layers of Mg atoms, O being at rest.	4	0·0412P − 0·33T	474	21·1
ν_7	Tangential oscillation of octahedral layers of Mg atoms, O being at rest.	8	0·0412P + 0·165T	428	23·4
ν_8	Normal oscillation of cubic planes, Mg and O atoms in opposite phases.	3	−0·794T	258	38·8
ν_9	Tangential oscillation of cubic planes, Mg and O atoms in same phase.	6	−0·397T	184	54·4

in the lower state and 668 cm.$^{-1}$ and 771 cm.$^{-1}$ in the upper state. We may reasonably expect to find frequencies of this order of magnitude also in the vibration spectrum of the crystal. Actually, all the investigators [Tolksdorf, (1928), Fock (*loc. cit.*), Barnes and Brattain (*loc. cit.*)] have found a strong absorption at about 14·2 μ (704 cm.$^{-1}$). Taking this to represent the fundamental of highest frequency, we may at once evaluate P, the larger of the two constants which we need to know. The second constant T may, as in the case of rocksalt, be expected to be quite small in comparison with P. The frequencies of the two lowest fundamentals are determined exclusively by the value of T, but as they are not directly accessible to observation, we have to choose T so as to fit the facts best over the whole range of the spectrum. Table I above shows the nine eigenfrequencies of MgO as calculated from the simplified formulæ of the preceding paper, with the atomic weights of oxygen and magnesium substituted for those of sodium and chlorine. The values of P and T adopted are shown at the head of the table.

3. Their Infra-Red Activities

If all the eigenvibrations are completely independent normal modes, only ν_3 which is the oscillation of the Mg and O lattices of atoms against each other would be active in infra-red absorption, and the rest would be inactive. As remarked already in the cases of diamond and rock-salt, such independence of the normal modes does not, as a matter of fact, subsist. On the other hand, there is clear evidence of the existence of a strong coupling between them due to anharmonicity and the finite amplitudes of vibration. As a consequence of this coupling, the activity of any mode results in an induced activity of the modes having frequencies not too greatly differing from it. On this basis, we should expect not merely ν_3, but also the higher and lower frequencies to be active in infra-red absorption. ν_8 and ν_9 in the table may however be expected to be more or less completely inactive by reason of their very low frequencies in comparison with ν_3.

Barnes and Brattain studied the reflecting power of an MgO crystal and found that it rises steeply from about 13 μ and shows a double maximum at 14·8 μ and 15·3 μ of about 65% in each case and then drops down again sharply. That the peak at 14·8 μ is itself the joint effect of more than one active frequency between 14 μ and 15 μ is clearly shown by their absorption curve for this region recorded with the thinnest of their five plates, as well as by that obtained with a layer of MgO fumed on to a plate of NaCl. As we shall see later, three summational frequencies $(\nu_5+\nu_9)$, $(\nu_7+\nu_8)$ and $(\nu_6+\nu_9)$ also fall in the vicinity, and it is therefore not surprising that a good deal of detail is observed in this region. There is however no difficulty in

recognising the presence in the absorption curves of two closely adjacent fundamental frequencies at about 14·15 μ and 14·55 μ respectively besides a third at 15·35 μ, in agreement with the indications of theory shown in Table I.

Strong (1931 *a*) studied the transmission through a film of MgO of infra-red radiations of selected wave-lengths obtained by means of crystal reflections. Table II exhibits his results.

TABLE II

Percentage Transmission by MgO Film

Wavelength in μ	6·7	8·7	20·75	22·9	27·3	29·4	32·8
Percentage Transmission	88	36	04	02	90	93	87

TABLE III

Percentage Reflection from MgO Crystal

Wavelength in μ	20·7	23	27·3	29·4	32·8	41	52	63
Percentage Reflection	80	72	44	42	35	33	32	31

In the same paper, Strong recorded the percentage of reflection by an MgO crystal at 22·9 μ and 32·8 μ as 80% and 33% respectively. In a later paper (1931 *b*) he gives fresh determinations over these and many more wave-lengths, and these are listed in Table III. The results obtained by Strong, *viz.*, practically complete absorption for 20·75 and 22·9 μ, and nearly total reflections at the same wave-lengths are what should be expected if there are fundamental frequencies at 21·1 μ and 23·4 μ as shown in Table I. The practically complete transparency for longer wave-lengths and the near identity of the reflecting power for such wave-lengths with the theoretical value of 27% given by the dielectric constant 9·8 are also significant. They are fully consistent with the *absence* of any fundamental frequency between 24 μ and 38 μ and the *inactivity* of the two lowest frequencies at 38·8 μ and 54·4 μ respectively.

Since Strong's observations indicate that the fundamental frequencies at 21·1 μ and 23·4 μ are strongly active, and since this activity is an induced effect, we should expect the fundamentals at 17·1 μ and 19·0 μ appearing in Table I to be still more strongly active, especially the one at 17·1 μ in view of its being adjacent in frequency to the " active " third fundamental. This indication is strikingly supported by the observations of Fock (1934). This

author, working with a film of MgO found that by far the strongest absorption in the whole wave-length region between 2μ and 40μ is at the wave-length $17{\cdot}3\mu$, and that the absorption falls off rapidly both towards longer and shorter wave-lengths. This observation shows clearly enough that $17{\cdot}3\mu$ is very close to an active fundamental. But it seems at first sight rather surprising that the activity of ν_4 should exceed that of ν_3 so notably. It may be recalled, however, that in the case of rocksalt, a similar situation but in the opposite direction arises, *viz.*, the peak of infra-red absorption by thin films is situated at ν_1 instead of at ν_3. One may therefore hazard the suggestion that the explanation is the same in both cases, the reversal as between NaCl and MgO being due to the fact that the metallic atom is the lighter in one case and the heavier in the other.

It may be remarked that no direct observation of the two lowest fundamentals ν_8 and ν_9 is possible since they are inactive. The fifth fundamental ν_5 falls on the steeply rising part of the transmission curve of Fock but is not indicated by any distinct peak of absorption. It is to be presumed therefore that its activity is rather low, possibly for the same reason that the activity of ν_4 is very high.

4. Analysis of the Absorption Curves

The range of wave-lengths covered by the observations of Barnes and Brattain includes besides 3 out of the 9 fundamentals, also 7 out of the 9 octaves, 34 out of the 36 possible summations of the frequencies taken two at a time, and nearly all of the 93 frequencies appearing in the third-order spectrum. It might seem at first sight scarcely possible to analyse an absorption spectrum including such a crowd of distinct frequencies. Various factors however simplify the task considerably, especially since the nine fundamental frequencies are known in advance with some precision. Firstly, the fundamental of highest frequency and its overtones fix the upper limits of frequency for the successive orders of spectra. Expressed in infra-red wave-lengths, these limits are $14{\cdot}2\mu$, $7{\cdot}1\mu$ and $4{\cdot}7\mu$ respectively. We do not therefore have to look for any fundamentals between 14·2 and $7{\cdot}1\mu$ or for second-order lines between $7{\cdot}1\mu$ and $4{\cdot}7\mu$. Intensity considerations are also very helpful. In a particular region of the spectrum, a fundamental may be expected to appear more strongly than an octave, an octave more strongly than a summation of two frequencies, a second-order frequency more strongly than one of the third-order, and so forth. Considerations of this kind are strongly supported by the observations recorded with the five plates of widely different thicknesses which enable us to assess the activity in absorption of the various frequencies. Comparison of the different

absorption curves shows, for instance, that with the thinnest plate of all (0·075 mm.), the first-order spectrum is strongly developed, the second-order spectrum appears rather weakly and the third-order spectrum still more weakly. With the next thicker plate (0·12 mm.), the first-order is completely blocked out, the second-order is very strongly developed, and the third-order is quite definitely present. With the plate of thickness 0·47 mm., the second-order spectrum is blocked out for wave-lengths greater than 10 μ, but for the wave-lengths between 7 μ and 9 μ where all the absorptions are necessarily weak, the observations with this plate as well as with the still thicker plate (1·75 mm.) are distinctly helpful.

The octaves of the fundamental frequencies are those most easily recognised in the absorption curves, and their observed positions furnish welcome confirmation of the correctness of the theoretically determined fundamental frequencies. $2\nu_7$, $2\nu_6$, $2\nu_5$ and $2\nu_4$ are seen very clearly in the absorption

TABLE IV

Calculated and Observed Absorption Frequencies

Sl. No.	Plate thickness	Wave-length Observed	Frequency Observed	Assignment	Calculated Frequency
	mm.	μ	cm.$^{-1}$		cm.$^{-1}$
1	0·075	15·4	651	ν_8	652
2	0·075	15·2	658	$\nu_6+\nu_9$	658
3	0·075	14·7	680	ν_2	680
4	0·075	14·4	694	$\nu_7+\nu_8$	686
5	0·075	14·2	704	ν_1	704
6	0·075	14·0	714	$\nu_5+\nu_9$	711
7	0·075	13·8	725	$\nu_6+\nu_8$	732
8	0·075	13·1	763	$\nu_4+\nu_9$	768
9	0·075	12·8	781	$\nu_5+\nu_8$	785
10	0·075	12·1	826	$\nu_3+\nu_9$	836
11	0·12	11·7	855	$2\nu_7$	856
12	0·075	11·6	862	$\nu_3+\nu_9$	864
13	0·12	11·15	897	$\nu_1+\nu_9$	888
14	0·12	10·9	917	$\nu_6+\nu_7$	902
15	0·075	10·7	935	$\nu_2+\nu_8$	938
16	0·12	10·5	952	$2\nu_6$	948
17	0·075	10·2	980	$\nu_1+\nu_8$	962
18	0·12	10·0	1000	$\nu_5+\nu_6$	1001
19	0·12	9·5	1053	$2\nu_5$	1054
20	0·12	9·3	1075	$\nu_3+\nu_7$	1080
21	0·12	9·0	1111	$\nu_4+\nu_5$	1111
22	0·075	8·8	1136	$\nu_1+\nu_7$	1132
23	1·75	8·7	1149	$\nu_2+\nu_6$	1154
24	0·12	8·5	1177	$2\nu_4$	1168
25	0·12	8·3	1205	$\nu_2+\nu_5$	1207
26	1·75	8·15	1227	$\nu_1+\nu_5$	1231
27	0·12	7·9	1266	$\nu_2+\nu_4$	1264
28	0·47	7·6	1316	$2\nu_3$	1304
29	1·75	7·3	1370	$2\nu_2$	1360
30	3·05	7·1	1408	$2\nu_1$	1408

curve of the plate 0·12 mm. thick. $2\nu_7$ is indicated by a complete cut-off in a small region of wave-lengths on either side of 11·7 μ. $2\nu_6$ is indicated by a very prominent dip in the curve at 10·5 μ. $2\nu_5$ is marked by a sharp and fairly prominent absorption line at 9·5 μ. $2\nu_4$ may also be made out at 8·5 μ, but appears much better developed as a deep trough at that position with the next thicker plate (0·47 mm.). A trough appears in the same curve at 7·6 μ which is the position of $2\nu_3$. A dip at 7·3 μ in the absorption curve for the plate of 1·75 millimetre thickness may be identified with $2\nu_2$, and the dip at 7·1 μ in the absorption curve of the thickest plate with $2\nu_1$.

The second-order combinations are much more numerous than the octaves, and hence it is not quite so easy to identify their appearance in the absorption curves. Especially, however, in the case of the two thinnest plates where the confusion arising from the superposition of the still more numerous third order combinations is not so serious, assignments may be made of the features observed in the absorption curves with some measure of confidence. Table IV is a collected list of 30 absorption lines in the first and second order spectra with their respective interpretations in terms of the nine fundamental frequencies.

5. Summary

The nine fundamental frequencies of the magnesium oxide structure are theoretically evaluated. Expressed as infra-red wave-lengths, they are respectively 14·2, 14·7, 15·35, 17·1, 19·0, 21·1, 23·4, 38·8 and 54·4 μ. All except the last two are active in the infra-red and their positions check very closely with the absorptions observed by Barnes and Brattain, by Strong and by Fock. The octaves of the first seven fundamentals and numerous summational frequencies including also the two inactive fundamentals have been identified with the lines recorded by Barnes and Brattain in the absorption spectrum of cleavage plates of various thicknesses.

Note added, 26th November 1947.—Deutschbein (*Annalen der Physik*, 1932, **14**, 712) found that a small percentage of chromic oxide can be successfully incorporated in MgO, thereby causing it to become luminescent when irradiated. The spectrum of this luminescence with the phosphor at room temperature, as also when it is cooled down to −195° C. has been investigated by him. At room temperature, a strong emission appears at λ 6991 in the red, with subsidiary bands symmetrically disposed about it on either side. These bands are due to the combination of the electronic transition at λ 6991 with vibrational transitions in the MgO structure, as is proved by the fact that at low temperatures the bands at shorter wave-lengths vanish, while those at longer wave-lengths persist. As the result of the cooling

the principal emission shifts to λ 6981 and becomes sharper, while the bands appearing at longer wave-lengths are resolved into a group of lines of varying intensities and widths in close juxtaposition. Other weaker electronic lines are also noticed in the vicinity of λ6981. These are found to be stronger with some samples of the luminescent material than with others differently prepared. Deutschbein's data for the samples which do *not* show these weaker lines at room temperature indicate that *all the subsidiaries exhibited at liquid air temperature* (other than the weak electronic transitions) are due to combination of the principal emission at λ 6981 with vibrational transitions in the MgO structure. The eigenfrequencies of MgO thus deduced are found to agree closely with the frequencies theoretically derived in the present paper. The diffuseness of the vibrational lines is accounted for by the width of the electronic line and the loading of the MgO lattice by the heavy atoms of chromium.

References

1. Barnes, Brattain and Seitz .. *Phys. Rev.*, 1935, **48**, 582.
2. Fock .. *Zeits. f. Phys.*, 1934, **90**, 44.
3. Mahanti, P. C. .. *Phys. Rev.*, 1932, **42**, 609.
4. Strong, (*a*) .. *Ibid.*, 1931, **37**, 1565.
5. ———— (*b*) .. *Ibid.*, 1931, **38**, 1818.
6. Tolksdorf .. *Zeits. f. Physik. Chemie.*, 1928, **132**, 161.

THE VIBRATION SPECTRA OF CRYSTALS

Part V. Lithium and Sodium Fluorides

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CONTENTS

1. Introduction. 2. Evaluation of the Eigenfrequencies. 3. Absorption and Reflection by Lithium Fluoride. 4. Absorption and Reflection by Sodium Fluoride. 5. Summary.

1. Introduction

Lithium and sodium fluorides are cubic crystals, their structure being of the NaCl type. The evaluation of their eigenfrequencies and the explanation of their spectroscopic behaviour are of particular interest for two reasons. Firstly, the low atomic weights of both the metal and the halogen and the strong interactions between the atoms in these fluorides result in their vibration spectra appearing at shorter wave-lengths than with all the other alkali halides. Secondly, as the result of the disparity in atomic weights of metal and halogen in lithium fluoride, the modes in which the fluorine atoms alone oscillate have much lower frequencies than those in which the lithium atoms alone or both lithium and fluorine atoms together oscillate. The atomic weights of sodium and fluorine do not differ so widely, and hence there is a closer approximation to each other of the various eigenfrequencies in the case of sodium fluoride. The spectroscopic behaviour of the two fluorides differs notably as the result of these circumstances.

2. Evaluation of the Eigenfrequencies

As in the cases of NaCl and MgO, the nine eigenfrequencies can be calculated from the simplified theoretical formula containing only two force-constants, one of which is much larger than the other. The large constant P is practically fixed by the highest of the nine eigenfrequencies, while the small constant T completely determines the two lower frequencies and notably influences also the intermediate ones. P can be found at once, while T is so chosen as to fit the spectroscopic facts best over the whole range of observation. Table I shows the evaluation for the case of lithium fluoride and Table II for the case of sodium fluoride, the values of P and T being in each case shown at the head of the table.

TABLE I. *Eigenfrequencies of Lithium Fluoride*

$P = 1{\cdot}02 \times 10^5$ dynes/cm. $T = -0{\cdot}015 \times 10^5$ dynes/cm. m_H is the mass of the hydrogen atom

Designation	Description of Mode	Degeneracy	$4\pi^2c^2m_H\cdot\nu^2$	Infra-red Wave-length
ν_1 ..	Normal oscillation of the cubic planes with *Li* and *F* atoms in same phase	3	$0{\cdot}197\ P-0{\cdot}34\ T$	16·9 μ
ν_2 ..	Tangential oscillation of the cubic planes with *Li* and *F* atoms in opposite phases	6	$0{\cdot}197\ P+0{\cdot}62\ T$	17·5 μ
ν_3 ..	Oscillation of *Li* and *F* lattices in opposite phase	3	$0{\cdot}197\ P+1{\cdot}58\ T$	18·2 μ
ν_4 ..	Normal oscillation of *Li* atoms in octahedral planes with *F* atoms at rest	4	$0{\cdot}144\ P-1{\cdot}15\ T$	19·0 μ
ν_5 ..	Tangential oscillation of *Li* atoms in octahedral planes with *F* atoms at rest	8	$0{\cdot}144\ P+0{\cdot}58\ T$	20·7 μ
ν_6 ..	Normal oscillation of *F* atoms in octahedral planes with *Li* atoms at rest	4	$0{\cdot}0527\ P-0{\cdot}42\ T$	31·4 μ
ν_7 ..	Tangential oscillation of *F* atoms in octahedral planes with *Li* atoms at rest	8	$0{\cdot}0527\ P+0{\cdot}21\ T$	34·2 μ
ν_8 ..	Normal oscillation of cubic planes with *Li* and *F* atoms in opposite phase	3	$-1{\cdot}23\ T$	56 μ
ν_9 ..	Tangential oscillation of Cubic planes with *Li* and *F* atoms in same phase	6	$-0{\cdot}62\ T$	80 μ

TABLE II. *Eigenfrequencies of Sodium Fluoride*

$P = 6{\cdot}82 \times 10^4$ dynes/cm. $T = -0{\cdot}10 \times 10^4$ dynes/cm. m_H is the mass of the hydrogen atom

Designation	Description of Mode	Degeneracy	$4\pi^2c^2m_H\nu^2$	Infra-red Wave-length
ν_1 ..	Normal oscillation of cubic planes with *Na* and *F* atoms in same phase.	3	$0{\cdot}0961\ P-0{\cdot}01\ T$	30·0 μ
ν_2 ..	Tangential oscillation of cubic planes with *Na* and *F* atoms in opposite phases	6	$0{\cdot}0961\ P+0{\cdot}38\ T$	30·9 μ
ν_3 ..	Oscillation of *Na* and *F* lattices in opposite phase.	3	$0{\cdot}0961\ P+0{\cdot}77\ T$	31·9 μ
ν_4 ..	Normal oscillation of *F* atoms in octahedral planes with *Na* atoms at rest.	4	$0{\cdot}0526\ P-0{\cdot}42\ T$	38·3 μ
ν_5 ..	Tangential oscillation of *F* atoms in octahedral planes with *Na* atoms at rest	8	$0{\cdot}0526\ P+0{\cdot}21\ T$	41·8 μ
ν_6 ..	Normal oscillation of *Na* atoms in octahedral planes with *F* atoms at rest.	4	$0{\cdot}0435\ P-0{\cdot}35\ T$	42·2 μ
ν_7 ..	Tangential oscillation of *Na* atoms in octahedral planes with *F* atoms at rest.	8	$0{\cdot}0435\ P+0{\cdot}17\ T$	45·9 μ
ν_8 ..	Normal oscillation of cubic planes with *Na* and *F* atoms in opposite phases	3	$-0{\cdot}76\ T$	87 μ
ν_9 ..	Tangential oscillation of cubic planes with *Na* and *F* atoms in same phase	6	$-0{\cdot}38\ T$	125 μ

3. Absorption and Reflection by Lithium Fluoride

Reinkober (1926) made some observations on the reflection and absorption of radiations in the near infra-red by lithium fluoride in the form of plates obtained by compressing the powder under high pressure. Later, Barnes (1932) studied the absorption curves in the remote infra-red by very thin films of the substance. The absorption, reflection and dispersion by single crystals has been investigated over a wide range of wave-lengths by Korth (1932) and by Hohls (1937). As the result of these various studies, we have a picture of the spectroscopic behaviour of lithium fluoride which can be interpreted in the light of the theoretical results.

Table I shows that $16{\cdot}9\,\mu$ is the shortest wave-length in the first-order spectrum. $8{\cdot}5\,\mu$ and $5{\cdot}6\,\mu$ would therefore be the shortest wave-lengths respectively in the second-order and third-order spectra of overtones and summations of the fundamental frequencies. We should accordingly expect a large increase in the absorption coefficient in passing from $5{\cdot}6\,\mu$ to $8{\cdot}5\,\mu$ and a further very large increase in passing from $8{\cdot}5\,\mu$ to $16{\cdot}9\,\mu$. The absorption measurements made by Hohls for various wavelengths and thicknesses fully support these indications of theory. Between $16\,\mu$ and $35\,\mu$ is a region of intense opacity as is to be expected. Hohls found a very weak but measurable transmission at $39\,\mu$ and a notably larger transmission at $41\,\mu$. The measurements likewise show that a steep rise in the reflecting power starts at about $14\,\mu$ and that a maximum of 78% is reached at $17\,\mu$. The reflection coefficient then diminishes a little and shows a minimum of 72% at $20\,\mu$. Beyond this wave-length it increases again and reaches a maximum value of 92% at $28\,\mu$. It then diminishes rapidly to 60% at $37\,\mu$ and to 38% at $40\,\mu$, beyond which the fall is more gradual. The measurements of absorption in very thin films made by Barnes likewise show that the strongest absorption is in the region of wave-lengths between $30\,\mu$ and $35\,\mu$, the peak appearing at $32{\cdot}6\,\mu$.

The facts recited above are readily understood on the basis that the first seven of the nine fundamentals listed in Table I are rendered strongly active by reason of their coupling with the so-called " active " mode ν_3, with the result that the whole range of wave-lengths between $16{\cdot}9\,\mu$ and $34{\cdot}2\,\mu$ is one of intense opacity. The sixth and seventh fundamentals ν_6 and ν_7 represent the oscillations of the fluorine atoms against each other, the lithium atoms remaining at rest. Whereas the first reflexion maximum between $15\,\mu$ and $20\,\mu$ is evidently due to the first five fundamentals which approximate to each other in frequency and form a group by themselves, the second reflection maximum between $20\,\mu$ and $40\,\mu$ is evidently due to ν_6 and

ν_7, as also to various overtones and summations of the fundamental frequencies falling within this wave-length range. It is evident from the appearance of this second maximum of reflection, as well as from the fact that the strongest absorption by thin films is at $32{\cdot}6\,\mu$ approximately midway between ν_6 and ν_7, that these two fundamentals are strongly active and indeed more so than any of the fundamentals of higher frequency. This is a remarkable but not altogether surprising result, since in the case of MgO we found that the oscillations of the oxygen atoms against each other give the maximum of infra-red absorption. The explanation of the effect is presumably the same as in the case of MgO.

4. Absorption and Reflection by Sodium Fluoride

The observations by Korth (*loc. cit.*) and by Hohls (*loc. cit.*) with crystal plates and of the absorption in thin films by Barnes (*loc. cit.*) give us the necessary data for the case of sodium fluoride. The clue to their understanding is likewise furnished by the activity of the eigenvibrations listed in Table II. In the present case, owing to the nearness of the atomic weights of sodium and fluorine, the four eigenfrequencies ν_4, ν_5, ν_6 and ν_7 form a group with their wave-lengths $38{\cdot}3\,\mu$, $41{\cdot}8\,\mu$, $42{\cdot}2\,\mu$ and $45{\cdot}9\,\mu$ fairly close to each other. Their octaves likewise form a close group, the wave-lengths being $19{\cdot}2\,\mu$, $20{\cdot}9\,\mu$, $21{\cdot}1\,\mu$ and $23\,\mu$. The absorption by thin films is a maximum at $40{\cdot}6\,\mu$, approximately midway between ν_4 and ν_5 which represent the oscillations of the fluorine atoms with the sodium atoms at rest. In this respect, the behaviour of sodium fluoride is analogous to that of lithium fluoride. On the other hand, there is only one reflection maximum instead of two as in lithium fluoride within the range of wave-lengths covered by the first-order spectrum. This maximum of 90% is located at $35\,\mu$ and is evidently the resultant effect of all the seven active fundamentals. The increase in reflecting power noticed for wave-lengths greater than 20 with μ a maximum of 48% at about $23\,\mu$ in the second-order spectrum is evidently due to the group of octaves lying in the vicinity. The increase in the absorption coefficient between $19\,\mu$ and $24\,\mu$ observed by Hohls is likewise due to the same cause. No such effects are noticed with lithium fluoride, since in the latter case, $2\nu_7$ lies within the first-order spectrum, while $2\nu_6$, $2\nu_5$ and $2\nu_4$ are widely separated from each other in the second-order spectrum. Hohls has however observed a minor peak in absorption at about $12{\cdot}9\,\mu$ which may be ascribed to several summationals falling in that region.

5. Summary

The eigenfrequencies of lithium and sodium fluorides have been theoretically evaluated and their observed spectroscopic behaviour is found to

be in accord with the results. The greater disparity in the atomic weights of metal and halogen in the case of lithium fluoride than in sodium fluoride leads to some interesting differences in behaviour between the two substances. In both cases, however, the frequency of maximum absorption does *not* correspond with the oscillation of the metal and halogen atoms against each other, but agrees with that of the oscillations in which only the fluorine atoms move, the metal atoms remaining at rest.

References

Barnes, R. B. .. *Zeits. fur Physik*, 1932, **75**, 723.

Hohls, H. W. .. *Annalen der Physik*, 1937, **29**, 433.

Korth .. 1932, quoted by Hohls.

Matossi, F. .. *Physikalische Zeitschrift*, 1932, **33**, 172.

Reinkober .. *Zeits. fur Physik.*, 1926, **39**, 437.

THE VIBRATION SPECTRA OF CRYSTALS

Part VI. Sylvine

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1. Introduction

The optical behaviour of sylvine shows clearly that the characteristic frequencies of atomic vibration lie more remotely in the infra-red than in the case of rock-salt. The question whether this is due solely to the atomic weight of potassium being greater than that of sodium or whether it is also partly due to a diminution in the strength of the interatomic forces is a point of considerable interest. The infra-red behaviour of sylvine has been studied by several investigators very thoroughly and their results furnish the data needed to decide this question. We shall accordingly proceed to evaluate the eigenfrequencies and to consider them in relation to the experimental facts. It may be remarked that some as yet unpublished work by Dr. R. S. Krishnan on the second-order spectrum of light-scattering in sylvine has assisted in determining the appropriate values of the force-constants.

2. The Nine Eigenfrequencies of Sylvine

As the atomic weight of chlorine is less than that of potassium, the two modes in which the chlorine atoms alone oscillate would have a higher frequency than the corresponding two modes in which the potassiums alone vibrate.

Table I

Eigenfrequencies of KCl

$P = 2{\cdot}30 \times 10^4$ dynes per cm.; $T = -0{\cdot}05 \times 10^4$ dynes per cm.

Designation	$4\pi^2c^2m_H{}^2\nu^2$	Frequency	Wave-length
		cm.$^{-1}$	μ
ν_1	0·0538P+0·00T	145	69
ν_2	0·0538P+0·214T	138	72
ν_3	0·0538P+0·430T	132	76
ν_4	0·0282P−0·226T	114	89
ν_5	0·0282P+0·113T	100	100
ν_6	0·0256P−0·205T	108	93
ν_7	0·0256P+0·102T	95	105
ν_8	−0·429T	60	167
ν_9	−0·214T	43	233

The difference in atomic weights (35.5 and 39) is however not large, and it follows that the frequencies of these four modes would not differ very much from each other and that the sequence in which they appear would depend on the precise values of the force constants. Table I shows the calculation of the frequencies. The values of P and T are both a little smaller than for rock-salt. For convenience, the symbols ν_4 and ν_5 have been used to designate the oscillations of the chlorine atoms while ν_6 and ν_7 designate those of the potassium atoms. It will be noticed, however, that ν_6 is greater than ν_5.

3. The Infra-Red Behaviour of Sylvine

The so-called "fundamental" oscillation in which the potassium and chlorine atoms move in opposite phases is ν_3 in our table, corresponding to an infra-red wave-length of 76 μ. It is to be remarked that this does not coincide either with the "rest-strahlen" wave-length of 63.4 μ or with the wave-length of 70.7 μ at which the maximum absorption is exhibited by the thinnest films (Barnes, 1932). It will be noticed that the latter is nearer ν_1 which has a wave-length of 69 μ. These remarks reinforce the point that owing to the anharmonicity and the mutual coupling of the various eigenvibrations, all of them must be considered to be active in greater or less degree, and that we must take account also of the activity of the various overtones and summations of the nine fundamental frequencies. On this basis, it is possible to understand the facts established by experimental study regarding the infra-red behaviour of sylvine.

Czerny (1930) investigated the reflecting power over the entire range of infra-red wave-lengths for which sylvine is opaque in moderate thicknesses. He found a small but quite definite swell in reflecting power in the wave-length range between 42 μ and 48 μ with a maximum of 20% at 46 μ. Referring to Table I, we recognize that this is the region in which the octaves of the fourth, fifth and sixth eigenfrequencies are grouped together, and the increase of reflection is therefore to be ascribed to their presence and conjoint effect. At 48 μ, the reflecting power reaches a minimum of 18% and then rises again steadily, reaching a maximum of about 90% in the range of wave-lengths 60–65 μ. It then falls down to 78% at 70 μ, 65% at 75 μ, 45% at 80 μ, 32% at 85 μ and 26% at 90 μ. The large increase in reflecting power in the range between 50 μ and 70 μ is a particularly noteworthy feature, and is readily understood when we recall that in this region lie numerous frequencies in the second-order spectrum, *viz.*, $2\nu_7$, $(\nu_6+\nu_9)$, $(\nu_5+\nu_9)$, $(\nu_4+\nu_9)$, $(\nu_3+\nu_9)$, $(\nu_2+\nu_9)$, $(\nu_1+\nu_9)$, $(\nu_7+\nu_8)$, $(\nu_6+\nu_8)$, $(\nu_5+\nu_8)$, $(\nu_4+\nu_8)$, $(\nu_3+\nu_8)$ and $(\nu_2+\nu_8)$. The fairly rapid drop of reflecting power at about 80 μ is an indication that the infra-red activity is considerable only

for the three highest fundamentals ν_1, ν_2, ν_3 and is relatively small for the fundamentals of lower frequency. The behaviour of sylvine in this respect is closely parallel to that of rock-salt.

Mentzel (1934) has very elaborately investigated the absorption coefficient of sylvine plates of various thicknesses over a wide range of wave-lengths. His work confirms the existence of the variations which we should expect in the range between 40 μ and 45 μ owing to the presence of the octaves of ν_3, ν_4 and ν_6 in that vicinity. The large drop in the absorption coefficient which occurs between 34 μ and 23 μ, and again between 23 μ and 17 μ is also readily understood, since 34 μ, 23 μ and 17 μ are respectively the shortest wavelengths in the second-order, third-order and fourth-order spectra.

4. Summary

The nine eigenfrequencies of sylvine are evaluated, and it is shown that the wave-length at which the maximum absorption is exhibited by very thin films is much nearer the first than the third of them which is the so-called active oscillation of the potassium against the chlorine atoms. The absorption and reflection data over the whole range of wave-lengths are in general accord with the indications of the theory. The force-constants for sylvine are a little smaller than for rock-salt.

References

1. Barnes .. *Zeit. f. Physik.*, 1932, **75**, 729.
2. Czerny .. *Ibid.*, 1930, **65**, 600.
3. Mentzel .. *Ibid.*, 1934, **88**, 178.

THE SCATTERING OF LIGHT IN DIAMOND AND ITS RAMAN SPECTRUM

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1. Introduction

Unlike many common solids, diamond cannot be had in large lumps for purposes of experimentation and one has to be satisfied with comparatively small specimens. In spite of this handicap, diamond offers such notable advantages that it is easily the best material which the physicist has at his disposal for testing theories of the spectroscopic behaviour of crystals and the scattering of light in them. In the first place, the elementary nature of diamond and the simplicity of its crystal structure make it possible to work out the consequences of any theory without excessive labour and thus obtain the data which could be compared with the experimental facts. Then again, the high refractive index of diamond and the fact that it is a valence crystal give it a large scattering power which make it possible to work with quite small specimens and yet obtain results. Further, the low atomic weight of carbon and the strength of the binding forces between the atoms result in spreading the vibration spectrum of the crystal over a wide range of frequencies. This is a feature which is highly advantageous in the critical study of Raman spectra. The frequency shifts being large, they appear widely dispersed and therefore well-resolved. Further, the greater part of the spectrum exhibiting the frequency shifts is recorded well away from the position of the exciting radiation which, unless it is completely eliminated, results with prolonged exposures in recording various spurious effects in its vicinity even with the best of instruments. Further, the fact that the vibration-frequencies are for the most part very high in the case of diamond has an important consequence namely that, except at the lowest end of the frequency range, the vibrations are not thermally excited to an appreciable extent. Secondary effects of thermal origin, *viz.*, the broadening and shifting of the Raman lines, which are of considerable importance in the case of many crystals even at ordinary temperatures, are hence negligible in the case of diamond. This has been clearly shown by the recent investigations of the author (Krishnan, 1946) on the temperature variations of the Raman frequencies of diamond. The width of the principal Raman

line with a frequency shift of 1332 cm.$^{-1}$ at room temperature is no more than that arising from instrumental and photographic factors, though at higher temperatures it broadens and has an easily measurable width.

To utilize to the fullest extent the advantages referred to above, it is necessary to work with non-luminescent diamonds. Such diamonds are also transparent in the ultra-violet and it becomes possible to employ the λ 2536·5 resonance radiation for exciting the Raman effect and thus take advantage of the intrinsic brightness of this radiation and its large scattering power arising from the λ^{-4} law. If the arc is effectively water-cooled and held against the wall of the tube with the aid of a magnet, the radiation is highly monochromatic and is free from any accompanying continuous spectrum. Incidentally also, by working in the ultra-violet, the larger dispersion and resolution of quartz spectrographs in that region are utilised. The importance of this in the study of Raman spectra exhibiting numerous closely spaced lines can scarcely be overstressed.

The use of an intense radiation for excitation is accompanied by certain complications, *viz.*, a general fogging of the photographic plate due to diffuse general illumination inside the spectrograph, as also spurious lines and wings in the immediate vicinity of the exciting line arising from diffraction effects present in any optical instrument, the intensity of which is directly proportional to the brightness of the exciting radiation falling on the slit. The special advantage of using the λ 2536·5 resonance radiation is that these spurious effects can, with care, be completely eliminated by absorbing the exciting radiation from the scattered light by a filter of mercury vapour. The filter can be made to work so effectively that the mercury line λ 2534·8 the intensity of which is extremely small compared to the λ 2536·5 resonance radiation appears stronger than its companion in the recorded spectra. In fact, when examined under high resolution the core of the resonance radiation is found to be completely removed.

Several investigations by the author on the Raman spectrum of diamond using the λ 2536·5 mercury resonance radiation as exciter have already been reported in earlier publications (R. S. Krishnan, 1944, 1945 and 1946). A notable advance has, however, been made possible by reason of a recent acquisition by Sir C. V. Raman of an exceptionally colourless plate of diamond of the non-luminescent type (N.C. 174). This has enabled the author to reinvestigate the scattering of light in diamond with a large Hilger (E1) quartz spectrograph and to obtain spectra which are fully resolved and the structure of which is exhibited without any ambiguity. Preliminary reports of the results have already appeared in *Nature* (Krishnan, 1947 *a*, *b*, *c*). Further details and a full discussion are presented in this paper.

2. Light-Scattering and Crystal Dynamics

The aim of the present investigation is the settlement of the fundamental question of the nature of the vibration spectra of crystals. The study of the scattering of light by the method of the Raman effect has proved its power so fully in other directions that one need scarcely doubt that it is the right method to settle also the problems of the solid state. In this connection, one may recall the pregnant remark made long ago by the late Lord Rutherford (1931) that the Raman effect " has proved, and will prove, an instrument of great power in the study of the theory of solids ". It will probably be useful before we proceed to describe the experimental results, to state the issues which need settlement and to consider them against the appropriate theoretical background.

Historically, the subject of the scattering of light in material media was first approached by theorists from two distinct points of view. The first point of view due to the late Lord Rayleigh, is that in which the individual particles of which the medium is composed, *e.g.*, the molecules of a gas, are considered to be the agents responsible for the phenomenon. The other point of view, first put forward by Einstein and later elaborated by Leon Brillouin, is that in which the medium is regarded as a continuum and the diffusion of light is ascribed to the " reflection " of the light waves by the sound waves of thermal origin assumed to be present and traversing it in all directions. Which of these two points of view is the more appropriate one clearly depends on the circumstances of the case, and is an issue to which experimental study is capable of returning a decided answer. For instance, in a gas, the Rayleigh point of view is the correct one, as is clearly shown by the fact that when we examine the light diffused by hydrogen gas with a Fabry-Perot etalon, we observe a broadening of the spectral lines which corresponds to the Maxwellian distribution of velocities of translation of the molecules (C. S. Venkateswaran, 1942 *a*). On the other hand, a similar examination of the light diffused by ethyl and methyl alcohol clearly shows a splitting of the spectral lines into two polarised components, their separation varying with the angle of observation (Sunanda Bai, 1942). Surprisingly enough, the same phenomenon is also observed in the highly viscous liquid glycerine (C. S. Venkateswaran, 1942 *b*). From these observations we shall certainly be justified in inferring that liquids exhibit a *coherent modified scattering of light* which may be regarded as a Raman effect due to pulsations of optical density occurring in phases definitely correlated with each other in adjacent volume elements of the medium. Alternatively, we may regard the spectral components as due to the Doppler shifts of frequency arising from the reflection of the light waves by moving sound waves. But

we would clearly not be justified in extending such notions to the consideration of the optical effects due to the rotations and vibrations of the molecules in a liquid. For explaining the large spectral shifts arising from such rotations and vibrations which are actually observed with liquids, we naturally go back to the Rayleigh point of view, and consider the individual particles in the medium as the responsible agents. For, the dynamics of such rotation and vibration is essentially a matter of the individual behaviour of the molecules, though indeed they may be influenced and partly modified by the interactions occurring between a molecule and its immediate neighbours.

Coming now to consider the case of crystals, it is a fact of observation that free and practically undamped propagation of elastic waves is possible in them. It is also known that in transparent crystals such waves give rise to optical effects whose strength is determined by their piezo-optic constants. There is therefore no reason to doubt that elastic waves of the three different possible kinds and of various wave-lengths, both larger and smaller than the wave-length of light, exist in crystals as the result of thermal agitation and that such waves give rise to optical stratifications of the same wave-length. But these optical stratifications cannot give rise to any observable scattering of light, unless their wave-length and orientation in relation to the direction of travel of the incident light waves is such as to give rise to a coherent reflection of the latter by the successive stratifications. The optical effects of all other stratifications would cancel out by interference. It follows *that the elastic waves of thermal origin would not give rise to any observable effect in the spectrum of light scattering*, except that which appears with small frequency shifts in the nature of Doppler effects in the immediate vicinity of the incident radiation.

While the continuum point of view is thus appropriate enough in considering the low frequency or elastic vibrations, dynamical principles and the observed experimental facts alike suggest that the particle point of view is the correct approach in respect of the vibrations of high frequencies appearing in the Raman spectrum. For, the high frequencies are themselves an indication that the vibrations are those of the individual atoms in the cells of the structure and not those of macroscopic volume elements in the crystal. Hence, the problem is one in particle dynamics analogous to the problem of the vibration spectra of polyatomic molecules and the results to be expected would be of a similar nature, *viz.*, a set of monochromatic frequencies, thus affording a natural explanation of the observed fact that crystals exhibit Raman spectra consisting of discrete lines. This is in fact, the approach to the subject made in the theory of the vibration spectra put forward by Sir C. V. Raman (1943), in which it is shown that a crystal containing *p*

atoms in each of its unit cells would have in general, $(24p-3)$ discrete frequencies of atomic vibration, though this number may be very considerably reduced by reason of the symmetry of the crystal.

On the other hand, the well-known theory of Debye, and the lattice theory of Born and Karman are both based on the belief that the ideas of continuum physics can be applied in respect of the high or infra-red frequencies of vibration of solids. In fact, the Born-Karman theory expressly assumes the existence of " optical waves " of such high frequencies. In the belief that a crystal containing N atoms necessarily possesses $3N$ *different* frequencies of vibration, the theory postulates also that the " optical wave-lengths " form a triply harmonic sequence in the same way as the acoustic wave-lengths. The vast majority of the wave-lengths thus assumed to exist are comparable with the lattice spacings of the crystal and as a consequence, the vibrations postulated in the theory have a diffuse continuous spectrum of frequencies spread over a wide range and not a set of discrete lines as actually observed in the Raman effect. An escape from this obvious contradiction with the facts is sought by means of the assumption that the entire continuous spectrum is rendered inaccessible to observation by reason of optical interference except only those frequencies which possess the right wave-length to give a coherent reflection, as in the case of the acoustic vibrations. We need not here stop to discuss the validity of this suggested explanation or the validity of the basic postulates on which the Born-Karman theory rests, since, as we shall see, the experimentally observed facts in the case of diamond give the answer to both of these questions. It will suffice here to state the points at issue which have to be settled by experiment.

I. Are the vibrations in crystals which manifest themselves in the Raman spectrum, " waves " extending through the volume of the crystal, or are they the vibrations of the atoms in the individual cells of the lattice ?

II. Is the complete vibration spectrum of the crystal in the infra-red region a continuous diffuse spectrum, or is it a discrete spectrum exhibiting a finite set of monochromatic frequencies ?

3. The Scattering of Light in Diamond

We shall now briefly describe the various features observed in a fully exposed spectrum of the scattered light in diamond. Using the Hilger medium spectrograph and the diamond of the ultra-violet transparent type (N.C. 174), numerous photographs were taken with exposures varying from a couple of seconds to several hours. The spectrum of diamond recorded with 2 minutes exposure is reproduced in Fig. 1 (*b*) together with the spectrum of the mercury arc [Fig. 1 (*a*)]. A heavily exposed spectrum recorded with

6 hours' exposure is shown in Fig. 2 (*b*). The Raman line with a frequency shift of 1332 cm.$^{-1}$ appeared on the plate with an exposure of only five seconds. Half a minute was needed to record the Doppler-shifted Brillouin components centred about the exciting radiation, the latter itself being effectively filtered out by a mercury vapour screen. See Fig. 1 (*b*). The same effect could be seen more clearly in the enlarged photographs reproduced in Figs. 1 (*c*) and (*d*) and in the microphotometric records shown in Figs. 1 (*e*) and (*f*). Half an hour's exposure sufficed to record the second-order Raman spectrum, while the anti-Stokes frequency shift of 1332 cm.$^{-1}$ appeared after forty-five minutes. An exposure of 3 hours resulted in heavily overexposing the second-order Raman spectrum, but was useful in bringing out the weak terminal line having a frequency shift of 2015 cm.$^{-1}$ which was liable to be overlooked with smaller exposures (see Fig. 3). Owing to the smaller dis-

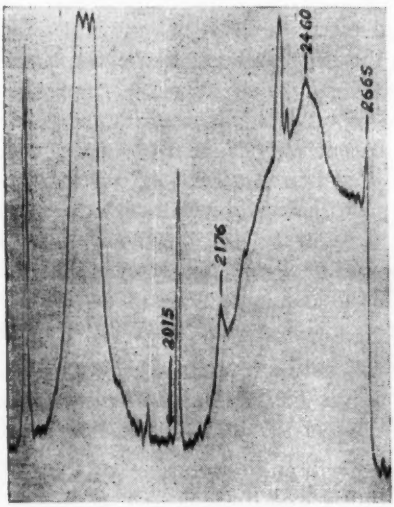


FIG. 3. Microphotometer record of the second order Raman spectrum of diamond showing the terminal line 2015 cm.^{1}

persion of the medium quartz spectrograph, the real nature of the second-order Raman spectrum of diamond is not exhibited as clearly as could be desired. The spectrum was therefore examined under the higher dispersion and resolution given by the Hilger (E1) large quartz spectrograph. Typical photographs recorded with different exposures are reproduced in Figs. 4 and 5. The principal feature noticeable in the spectra is the appearance of a whole series of sharply defined Raman lines clearly resolved from each

other. Longer exposures up to 10 hours taken with the medium quartz spectrograph revealed no new features except a couple of fainter lines in the spectrogram. These fainter lines have been identified as the 1332 Raman line excited by the feeble mercury lines. It is very significant that no hint or trace of the continuous spectrum of elastic vibrations forming the so-called " acoustic branches " of the lattice spectrum of the crystal appears on the plate even with the longest exposures. These facts will be evident from a comparison of Figs. 2 (*a*) and (*b*).

From the experimental facts stated above, it is clear that the parts of the vibration spectrum of diamond in the lower and upper ranges of frequency differ radically in their behaviour. The first part is totally inactive in light-scattering, while the second part is strongly Raman-active, giving an intense second-order spectrum. The character of the spectrum is also totally different in the two ranges of frequency. While the spectrum of the elastic vibrations is necessarily a continuous one, the discrete nature of the atomic vibration spectrum in the upper ranges of frequency is clearly manifested in the second-order Raman effect; the overtones and summations of the primary vibration frequencies appear under adequate instrumental power clearly resolved into numerous closely spaced sharp lines. These differences are fundamental and compel us to recognize that the two parts of the vibration spectrum are physically of a different nature. In the lower ranges of frequency, we are concerned with elastic waves traversing the crystal from end to end and forming stationary wave-patterns, while in the upper ranges of frequency, we are concerned with the vibration of the atoms in the individual cells of the crystal lattice. The spectroscopic facts thus give a decisive answer to the theoretical issues stated at the end of the preceding section. They show that the assumptions on which the Debye and Born-Karman theories are based are unjustified and that the conclusions regarding the nature of the atomic vibration spectra to which those theories lead are altogether untenable.

4. The Doppler-shifted Components

The magnitude of the frequency shifts.—As already indicated in the last section, the spectrum of the light scattered by diamond when examined with a medium quartz spectrograph using a fine slit exhibits a doubling of the $\lambda 2536{\cdot}5$ line, the latter itself being completely quenched by a mercury vapour filter (see Fig. 1). The doubling is in the nature of a Doppler effect arising from the selective reflection of the monochromatic light by the approaching and receding sound waves of thermal origin in the medium. The components are called Doppler-shifted components and are sometimes

known as Brillouin components. Their frequency shift from the exciting line is given by the formula due to Brillouin

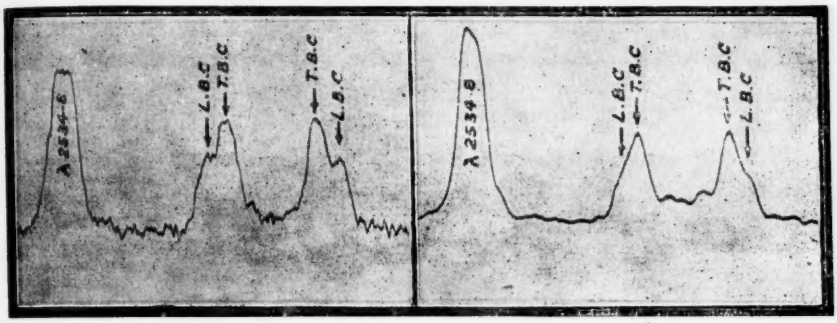
$$\Delta\nu = \pm 2\nu \frac{v}{c}\mu \sin \theta/2, \qquad (1)$$

where ν, μ, v and c are respectively the frequency of the incident radiation, refractive index of the medium, velocity of sound in the medium and the velocity of light. θ is the angle of scattering. This is the first time that the existence of sound waves of thermal origin in a solid has been demonstrated without the use of interferometers. The success is mainly due to the fact that the velocity of sound and the refractive index of diamond have high values. The resulting Doppler displacements in the frequency of the λ 2536·5 radiation scattered transversely in diamond are large enough to be recorded directly without interferometric aid using a quartz spectrograph of moderate power.

It is well known that for any given direction in a crystal, there are in general three distinct sound velocities, one longitudinal and two transverse. One should therefore expect to observe six Doppler-shifted components three on either side of the exciting radiation. The spectrogram taken with diamond N.C. 174 and the medium quartz spectrograph, and reproduced in Fig. 1 (*b*) exhibited only two Brillouin components. This might be due to the small dispersion of the spectrograph. Moreover, diamond N.C. 174 had curved edges and as such, it was not quite suited for making a quantitative verification of equation (1) and also for investigating the directional variation of the velocity of sound in diamond. Another specimen of diamond of the non-luminescent ultra-violet transparent type, namely N.C. 60, was therefore chosen for the present investigation. It was in the form of a rectangular plate (10 × 6 × 1·5 mm.) with faces and edges well polished. X-ray diffraction studies (Ramachandran, 1946) indicated that the length, breadth and thickness of the diamond N.C. 60 were parallel to $01\bar{1}$, 111 and $\bar{2}11$ directions. As the specimen was slightly yellowish in colour, its transparency to the λ 2536·5 radiation was definitely less than that of N.C. 174.

Diamond N.C. 60 was clamped with its faces vertical and facing a vertical quartz mercury arc of special design. The light scattered in the transverse horizontal direction and emerging out of the smaller edge was focussed on the slit of a Hilger E1 large quartz spectrograph. The spectrum was photographed with exposures of the order of six hours using a slit width of 0·02 mm. A typical spectrogram together with a comparison spectrum of the mercury arc is reproduced in Fig. 6. In the spectrum of the direct arc the λ 2536·5 line has been completely absorbed. In the

scattered spectrum, on the other hand, one observes four displaced components which are more clearly seen in the enlarged photograph and the microphotometer record reproduced in Figs. 7 (*a*) and 8 (*a*) respectively. The



a *b*

FIG. 8. Microphotometer records of thermal scattering in diamond for two different orientations: *L.B.C.* = longitudinal Brillouin components; *T.B.C.* = transverse Brillouin components.

frequency shifts of the two pairs of Brillouin components are $\pm 8{\cdot}8$ cm.$^{-1}$ and $\pm 5{\cdot}4$ cm.$^{-1}$ and the corresponding values of the velocity of sound calculated from equation (1) are 18,080 and 11,000 metres per second. μ is taken as 2·61 for λ 2536·5. It follows therefore that the outer pair of components arise from the longitudinal sound waves in diamond, while the inner brighter ones are due to the transverse sound waves. Unlike in many other crystals, the transverse components in diamond are brighter than the longitudinal components. The Doppler-shifted components have a finite width which might be attributed to the fact that the light incident on the plate of diamond was a convergent beam with a semi-angle of convergence of the order of 15°. The angle of scattering, θ, had a mean value of 90°.

Determination of the sound velocities in diamond.—For a cubic crystal, the squares of the three possible velocities for a sound wave travelling in a direction whose direction cosines are l, m and n are given by the three roots of v^2 in the following determinantal equation:—

$$\begin{vmatrix} c_{11}l^2 + c_{44}(m^2+n^2) - \rho v^2 & (c_{12}+c_{44})\,lm & (c_{12}+c_{44})\,ln \\ (c_{12}+c_{44})\,ml & c_{11}m^2 + c_{44}(l^2+n^2) - \rho v^2 & (c_{12}+c_{44})\,mn \\ (c_{12}+c_{44})\,nl & (c_{12}+c_{44})\,nm & c_{11}n^2 + c_{44}(l^2+m^2) - \rho v^2 \end{vmatrix} = 0 \quad (2)$$

where c_{11}, c_{12} and c_{44} are the three elastic constants and ρ the density. Using the values of the elastic constants of diamond obtained by Bhagavantam and Bhimasenachar (1946) by the ultra-sonic method, namely $c_{11}=9{\cdot}5 \times 10^{12}$

dynes/cm.^{2}, $c_{12} = 3{\cdot}9 \times 10^{12}$ dynes/cm.^{2} and $c_{44} = 4{\cdot}3 \times 10^{12}$ dynes/cm.^{2}, the values of the three possible sound velocities along specific directions perpendicular to the cubic axis, the dodecahedral axis and the octahedral axis in diamond have been evaluated. The variation of sound velocity with direction along the three sections has been graphically represented in Figs. 9, 10 and 11. A comparative study of these curves shows that the

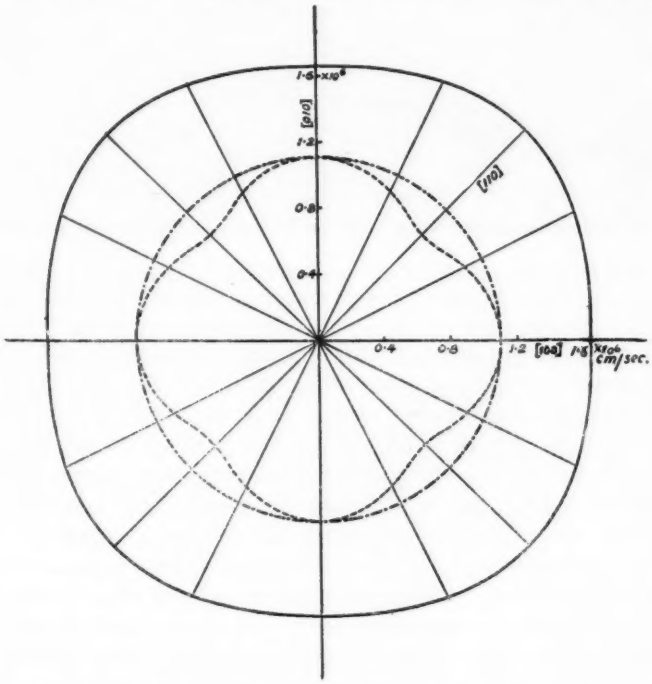


FIG. 9. Directional variation of sound velocities in diamond; section perpendicular to the cubic axis. Continnous curve refers to longitudinal sound waves and broken curves to transverse sound waves.

two sets of transverse sound waves in diamond have very nearly the same velocity in all the directions. The maximum difference is along the dodecahedral axis, the velocities for the transverse waves being equal to 11,080 and 8,950 metres per second. This is why only one pair of transverse Brillouin components is recorded in the scattered spectrum of diamond. The longitudinal sound waves have the maximum velocity of 18,120 metres per second along the octahedral axis and the minimum velocity of 16,500 metres per second along the cubic axis.

In order to study the directional variation of sound velocity in diamond, the transversely scattered light was photographed using the large quartz spectrograph for different orientations of diamond (N.C. 60) with reference to the directions of illumination and observation. Enlarged photographs showing the Doppler shifted components corresponding to three different settings of the diamond are reproduced in Fig. 7 and two microphotometric

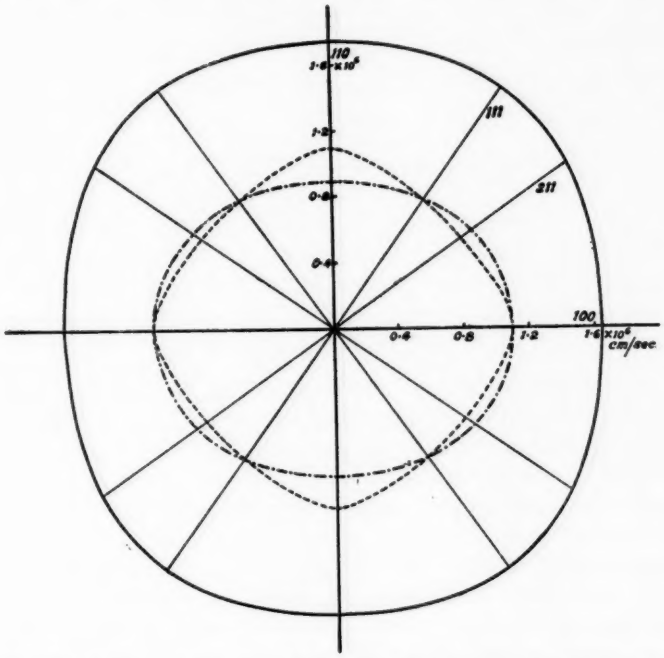


FIG. 10. Directional variation of sound velocities in diamond; section perpendicular t the dodecahedral axis.

records are included in Fig. 8. As is evident from the reproduced photographs, one observes only four Doppler-shifted components in light-scattering in diamond, one pair each due to longitudinal and transverse sound waves. The pair due to transverse sound waves is always brighter than the longitudinal components.

From a comparative study of the photographs reproduced in Fig. 7 and the microphotometric records in Fig. 8, it becomes evident that the velocity of sound waves varies with direction inside the diamond. For example, for the second setting, the inner and outer components are les

clearly separated from each other than for the other two settings, showing thereby that the velocities of longitudinal and transverse waves are nearer to each other in the second case than in the other two cases. Interchanging the directions of illumination and observation for a given setting of the plate of diamond did not change the nature of the pattern obtained.

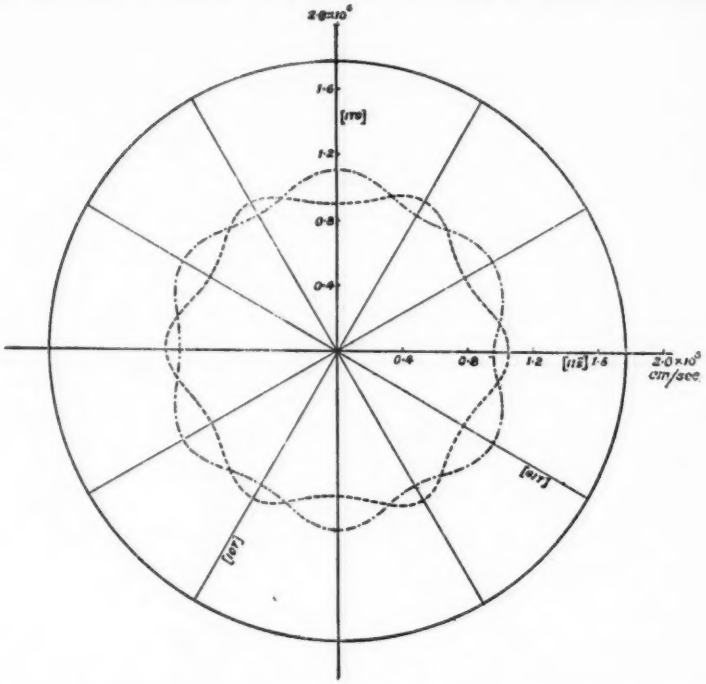


FIG. 11. Directional variation of sound velocities in diamond; section perpendicular to the octahedral axis.

The frequency shifts of the longitudinal and transverse Brillouin components for the three different orientations of the diamond have been measured and the corresponding sound velocities have been evaluated. The values are entered in Table I. The theoretical values of the velocities of longitudinal and transverse sound waves corresponding to the first two settings of the diamond could be read off from the curves reproduced in Figs. 11 and 10. For the third setting the values were calculated directly from the known elastic constants of diamond. The agreement between the experimental and theoretical values of the velocity of sound in diamond is fairly satisfactory.

TABLE I

Setting	Incident beam parallel to	Direction of observation parallel to	Plane of Scattering parallel to	Nature of the Brillouin component	Frequency shift in cm.$^{-1}$	Velocity of sound in metres/sec.	
						Observed	Calculated
1	$\bar{2}11$	$01\bar{1}$	(111)	Longitudinal	±8·8	18,080	17,800
	$\bar{2}11$	$01\bar{1}$	(111)	Transverse	±5·4	11,000	10,300 9,800
2	$\bar{2}11$	111	$(01\bar{1})$	Longitudinal	±8·0	16,400	16,500
	$\bar{2}11$	111	$(01\bar{1})$	Transverse	±5·6	11,500	11,000 10,600
3	$01\bar{1}$	111	$(\bar{2}11)$	Longitudinal	±8·5	17,500	17,300
	$01\bar{1}$	111	$(\bar{2}11)$	Transverse	±5·5	11,200	10,500

Intensity of the Brillouin components.—Leontowitsch and Mandelstamm (1932) derived a formula for the intensity of the light reflected or transversely scattered by sound waves of thermal origin in the medium

$$I = \frac{\pi^2}{2\lambda^4} kT\mu^8 \left\{ \frac{2(p_{12}^2 + p_{44}^2)}{c_{11} + c_{12} + 2c_{44}} + \frac{p_{44}^2}{c_{44}} \right\} \qquad (3)$$

where I is the intensity of light sattered by 1 cm.^{3} of the substance for natural light of unit intensity, λ the wave-length of light, μ the refractive index, c_{ik} elastic constants, p_{ik} Pockels' elasto-optical constants and T the temperature of the scattering substance. According to Hans Mueller's analysis (1938), the first term inside the double brackets is the contribution due to longitudinal sound waves, while the second term represents the contribution due to the transverse sound waves. The values of the elasto-optical constants for diamond as determined by G. N. Ramachandran (1947) are $p_{11} = 0{\cdot}125$, $p_{12} = -0{\cdot}325$ and $p_{44} = 0{\cdot}11$. Putting these values of p_{ik} and the values of c_{ik} as determined by Bhagavantam and Bhimasenachar (1946) in equation (3), the contributions due to the longitudinal and transverse sound waves to the intensity of thermal scattering in diamond have been evaluated. The intensities of the longitudinal and transverse Brillouin components are respectively $1{\cdot}14 \times 10^{-5}$ and $0{\cdot}31 \times 10^{-5}$ for incident light of unit intensity. Thus according to the formula of Leontowitsch and Mandelstamm, the longitudinal components should be about four times more intense than the sum of the transverse components. This is in complete contradiction with the experimental observation, namely that the transverse Brillouin components are much brighter than the longitudinal components (see Figs. 7 and 8). The subject therefore requires further investigation.

Temperature dependence of intensity.—According to Leontowitsch and Mandelstamm's formula, the intensity of thermal scattering is directly proportional to the absolute temperature. In order to verify this result in the case of diamond the following procedure was adopted. For work above room temperature, a specially designed heater similar to the one described by the author in one of the earlier publications (Krishnan, 1946) was used. With the aid of a quartz medium spectrograph and diamond N.C. 174 two photographs of the scattered spectrum were taken on the same negative, one with the crystal maintained at room temperature, *i.e.*, 305° T. and the other at 570° T. For work below room temperature, a demountable Dewar flask with quartz windows was used. A mixture of solid carbon dioxide and alcohol formed the refrigerant for one observation below the room temperature, and liquid air for a second observation. Using the above arrangement the scattered light was photographed with the diamond maintained successively at 175° T. and 85° T.

The intensities of the Doppler-shifted components are markedly influenced by temperature. This is beautifully illustrated by the series of photographs reproduced in Fig. 12 (*a*) to (*d*). They represent the spectra of the scattered light taken with the diamond maintained successively at 570°, 305°, 175° and 85° T. The corresponding enlargements showing the Doppler shifted components and the companion mercury line λ 2534·8 are reproduced in Figs. 12 (*e*) to (*h*). It will be noticed from the reproductions that in contrast with the 1332 Raman line the intensity of which is practically unaffected by the change of temperature of the diamond, the Doppler-components become rapidly weaker with falling temperature. This is to be expected on theoretical grounds, since for the Doppler-shifted components $h\nu_s \ll kT$ while for the Raman line $h\nu_r \gg kT$. At room temperature, *i.e.*, at 305° T. the aggregate intensity of all the Doppler shifted components is less than one fourth the intensity of the Raman line.

5. First-order Raman Spectrum

Only a single Raman line with frequency shift of 1332·0 cm.$^{-1}$ appears in the first order spectrum of diamond. This frequency represents the fundamental vibration of the diamond structure, *viz.*, the triply degenerate mode in which the two interpenetrating Bravais lattices of carbon atoms oscillate against each other. Longer exposures did not exhibit any Raman line having a frequency shift less than 1332 cm.$^{-1}$ except a couple of fainter lines which appeared in the region of low frequency shifts and were identified as the 1332 Raman line excited by the feeble mercury lines on the shorter wavelength side of λ 2536·5. The appearance of a single Raman line in the first

order spectrum of diamond is a direct consequence of the high symmetry of its crystal structure. It is found that there is no measurable difference in the frequency shifts of the principal Raman line in the spectra of the ultra-violet transparent and opaque types of diamond.

6. The Second-Order Raman Spectrum

The true nature of the second-order spectrum of diamond is exhibited unambiguously in the series of photographs reproduced in Figs. 4 and 5. These represent the prints enlarged from different spectrograms taken with a Hilger E1 large quartz spectrograph and diamond N.C. 174. The exposures used varied from 12 hours to a maximum of 4 days. The greater dispersion and resolution of the large quartz spectrograph have enabled the author to bring out the salient features of the second-order spectrum more clearly than was possible in the previous investigations. The most striking feature noticeable in the spectra is the appearance of a whole series of sharply defined Raman lines clearly resolved from one another. The prominent ones have been marked in Figs. 4 and 5 with their respective frequency shifts in wave numbers from the exciting line. The terminal line with a frequency 2015 cm.$^{-1}$ is more clearly seen in the microphotometer record reproduced in Fig. 3. The width of the individual Raman lines, as is evident from a comparison with the lines of the mercury arc, is no greater than that arising from the instrumental and photographic factors. Besides the Raman lines whose positions are marked in Figs. 4 and 5, there are other fainter lines just discernible in the spectrogram against a fainter unresolved background of apparently continuous spectrum. These faint lines are more clearly seen as small kinks in the microphotometer records reproduced in Fig. 13. That they are genuine Raman lines and are not due to chance fluctuations has been verified by comparing the microphotometer records taken at different regions on the same negative and with different spectrograms. Three typical records are reproduced in Fig. 13. The positions of the fainter lines are marked in the figure.

The second-order Raman lines of diamond are listed in Table II together with their frequency shifts in wavenumbers from the exciting line and their widths in wavenumbers. Taking the intensity of the most intense line as 15 arbitrary units, the intensities of the remaining lines have been estimated and the values are included in Table II. Excluding the two terminal Raman lines with frequency shifts 2665·4 cm.$^{-1}$ and 2015 cm.$^{-1}$, the Raman lines in the second-order spectrum of diamond can be classified into three groups.

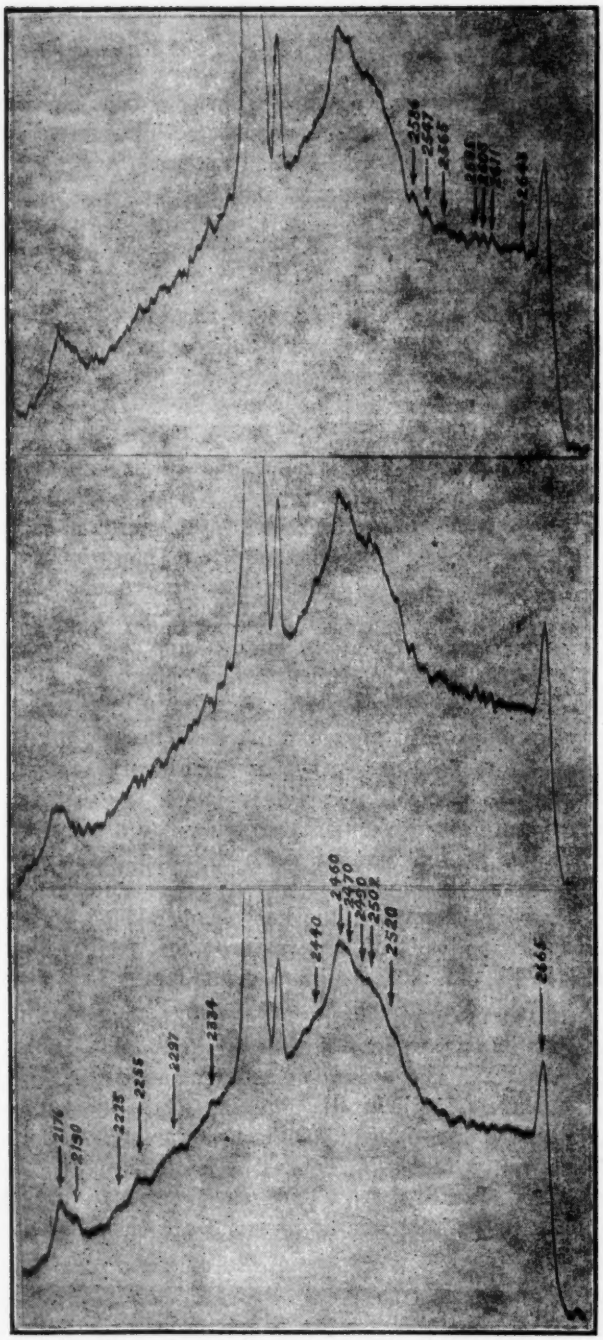


FIG. 13. Microphotometer records of the second order Raman spectrum of diamond taken with the Hilger E 1 large quartz spectrograph.

TABLE II

No.	Frequency shift in cm.$^{-1}$ (Observed)	Width in cm.$^{-1}$	Relative intensity	Assignment	Frequency shift in cm.$^{-1}$ (Calculated)
1	2015	3	1	Octave, $2\nu_6$	
2	2176	4	5	Octave, $2\nu_5$	
3	2190		3		
4	2225	3	3	Combination, $\nu_4+\nu_5$	2237
5	2255	5	6	Combination, $\nu_2+\nu_6$	2258
6	2297	4	7	Octave, $2\nu_4$	
7	2334	4	8	Combination, $\nu_2+\nu_5$	2338
8	2440	4	10	Octave, $2\nu_3$	
9	2460	3	15		
10	2470	3	15		
11	2490	4	12	Octave, $2\nu_2$	
12	2502	4	12		
13	2520	4	9		
14	2536	3	4		
15	2547				
16	2565			Combination, $\nu_1+\nu_3$	2564
17	2595				
18	2603				
19	2611				
20	2643				
21	2665·4	4	10	Octave, $2\nu_1$	

The first group which lies on the longer wavelength side of the mercury line λ 2698·9, consists of six very sharp, intense and closely spaced lines with frequency shifts ranging from 2440 cm.$^{-1}$ to 2520 cm.$^{-1}$. It is interesting to note that most of the lines of this group are more intense than the 2665·4 line. The second group consists of six Raman lines of moderate intensity and sharpness with frequency shifts ranging from 2176 to 2334 cm.$^{-1}$ lying on the shorter wavelength side of λ 2698·9. The third group comprises half a dozen feeble lines imperfectly resolved and appearing in the region of frequency shifts bounded by the 2520 and 2665·4 Raman lines.

As already pointed out in section 4, the discrete character of the second-order Raman spectrum is a contradiction of the conclusions regarding the nature of the atomic vibration spectra of crystals to which the theories of Debye and Born lead. The appearance of several discrete frequencies in the second order spectrum of diamond, on the other hand, finds a natural explanation in the new theory of lattice dynamics put forward by Sir C. V. Raman. According to the Raman theory, diamond has nine fundamental modes of oscillation of which two have identical frequencies. The vibration spectrum of diamond has therefore eight numerically different vibration frequencies. If ν_1, ν_2, ν_3, ν_4, ν_5, ν_6, ν_7 and ν_8 are the frequencies arranged in the descending order of magnitude, their degeneracies are respectively 3, 8, 6, 4, 3 + 3, 4, 6 and 8. Of these, the highest frequency corresponds

to the triply degenerate vibrations of the two interpenetrating Bravais lattices of carbon atoms and is active in the Raman effect. It has a value of 1332 cm.$^{-1}$ The other seven frequencies represent the oscillations of the layers of carbon atoms parallel to the faces of the octahedron or cube occurring normal or tangential to these planes with the phases reversed at each successive equivalent layer. All these seven modes are inactive in the Raman effect as fundamentals. They may, however, appear in the second-order Raman spectrum as octaves and combinations.

Coming now to the identification of the Raman lines appearing in the second-order spectrum, the terminal line with a frequency shift of 2665 cm.$^{-1}$ is obviously the octave of the principal mode of oscillation. It is important to note that the frequency shift of this line is very nearly double that of the 1332 Raman line. This fact suggests that the mechanical anharmonicity factor for this particular mode of vibration is small. From theoretical considerations based on the intensities of the Raman lines, it is possible to identify the lines with frequency shifts 2502, 2460, 2297, 2176 and 2105 cm.$^{-1}$ as octaves of the modes of vibration ν_2, ν_3, ν_4, ν_5 and ν_6 respectively. See the papers by Sir C. V. Raman (1947) and by K. G. Ramanathan (1947) appearing in this Symposium. The remaining two modes, namely ν_7 and ν_8 have low frequencies and their octaves are not observed in the second-order spectrum. The frequencies in wavenumbers of the first six modes are as follows:—$\nu_1 = 1332$, $\nu_2 = 1250$, $\nu_3 = 1232$, $\nu_4 = 1149$, $\nu_5 = 1088$ and $\nu_6 = 1008$ cm.$^{-1}$ On the basis of the above identification, the Raman lines with frequency shifts 2225, 2255, 2334 and 2565 cm.$^{-1}$ can be satisfactorily explained as combinations and the calculated values of their frequency shifts are entered in column 6 of Table II. There remain only five more prominent lines with frequency shifts 2190, 2440, 2470, 2490 and 2520 for the appearance of which a satisfactory explanation has to be found. From an examination of the second-order spectrum reproduced in Fig. 4, it will be seen that the first one falls in the vicinity of the 2176 line ($2\nu_5$), the next two fall on either side of the 2460 line ($2\nu_3$) and the last two fall on either side of the 2502 line ($2\nu_2$), forming in all three sets of which the second and the third almost run into each other. The only rational explanation appears to be that since ν_2, ν_3 and ν_5 are highly degenerate oscillations, the degeneracy is partly removed by the anharmonicity resulting in the splitting of the octaves into two or more components. Similar effects have been observed in the case of polyatomic molecules. Certain energy levels that coincide in the harmonic oscillator approximation split into a number of levels when anharmonicity is taken into consideration. In other words, when second-order effects are taken into account, the high degeneracy of the fundamental vibration does

not remain, but a splitting occurs due to anharmonicity. Splitting of the octaves of ν_2 and ν_3 may in part be attributed to resonance effect arising from the fact that these two vibrations have very nearly the same frequency and that combinations $\nu_1 + \nu_4$ and $\nu_2 + \nu_3$ fall roughly in the region of the octaves.

The author is grateful to Professor Sir C. V. Raman, F.R.S., for the loan of the diamonds used in the present investigation and also for suggestions and encouragement.

7. Summary

A detailed study of the scattering of light in diamond and its Raman spectrum has been made using the $\lambda 2536 \cdot 5$ mercury resonance radiation as exciter. The scattered spectrum exhibits two pairs of Doppler-shifted components, one pair due to the longitudinal sound waves, and the other due to the two sets of transverse sound waves which have very nearly the same velocity. The velocities of the longitudinal and transverse sound waves estimated from the observed frequency shifts of the displaced components are in agreement with those calculated from the elastic constants of diamond. The directional dependence of sound velocity in diamond has been quantitatively verified. Contrary to expectation, the longitudinal Doppler components are found to be less intense than the transverse Doppler components.

The second-order spectrum of diamond has been examined with a quartz spectrograph of high dispersion and resolution. It exhibits a whole series of sharply defined Raman lines the frequency shifts of which have been tabulated. The prominent ones which are 15 in number have been satisfactorily explained as octaves or combinations of six of the eight fundamental frequencies of vibration of the diamond lattice to be expected on the basis of the Raman theory, some of which are split due to the removal of degeneracy by anharmonicity and due to resonance effect.

References

Raman Effect Studies

1. Bhagavantam, S. .. *Ind. Journ. Phys.*, 1930, **5**, 169 & 573.
2. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, A, 1944, **19**, 216 & 298.
——— .. *Nature*, 1945, **155**, 171.
——— .. *Proc. Ind. Acad. Sci.*, A, 1946, **24**, 25 & 40.
——— .. *Nature*, 1947 *a*, **159**, 60.
——— .. *Ibid.*, 1947 *b*, **159**, 740.
——— .. *Ibid.*, 1947 *c*, **160**, 230.
3. Nayar, P. G. N. .. *Proc. Ind. Acad. Sci.*, 1941, **13**, 483.

4. Ramaswamy, C. .. *Nature*, 1930, **125**, 704.
———— .. *Ind. Journ. Phys.*, 1930, **5**, 97.
5. Robertson and Fox .. *Nature*, London, 1930, **125**, 704.
——, Fox and Martin *Phil. Trans. Roy. Soc.*, A, 1934, **232**, 463.

General

6. Bhagavantam, S., and Bhimasenachar, J. .. *Proc. Roy. Soc.*, A, 1946, **187**, 381.
7. Leontowitsch, M., and Mandelstamm, S. *Phys. Z. Sowjet.*, 1932, **1**, 317.
8. Müller, H. .. *Proc. Roy. Soc.*, 1938, **166**, 425.
9. Ramachandran, G. N. *Proc. Ind. Acad. Sci.*, A, 1946, **24**, 95.
———— .. *Ibid.*, 1947, **25**, 208.
10. Raman, C. V. .. *Ibid.*, 1943, **18**, 237.
———— .. *Ibid.*, 1947, **26**, 356.
11. Ramanathan, K. G... *Ibid.*, 1947, **26**, 481.
12. Rutherford, E. .. *Proc. Roy. Soc.*, 1931, **130**, 239.
13. Sunanda Bai .. *Proc. Ind. Acad. Sci.*, A, 1942, **15**, 349.
14. Venkateswaran, C. S. *Ibid.*, 1942 *a*, **15**, 316; 1942 (*b*), **15**, 322.

Description of Plates

Plate IX

Fig. 1. (*a*) Filtered mercury spectrum taken with a medium quartz spectrograph.
(*c*) and (*e*) Enlargement and microphotometer record respectively showing λ 2534·8 and the wings of λ 2536·5.
(*b*) Raman spectrum of diamond showing the Brillouin components (B.C.) and the 1332 Raman line.
(*d*) and (*f*) enlargement and microphotometer record of the Brillouin components.

Plate X

Fig. 2. (*a*) Filtered mercury spectrum taken with a medium quartz spectrograph.
(*b*) Heavily exposed Raman spectrum of diamond.

Fig. 6. Raman spectrum of diamond showing the Brillouin components and the 1332 Raman line taken with a large quartz spectrograph (E1) together with a comparison spectrum of the mercury arc.

Plate XI

Figs. 4–5. Second-order Raman spectrum of diamond taken with E1 quartz spectrograph. Enlarged from different negatives.

Plate XII

Fig. 7. Enlargements showing the Doppler-shifted components and the companion mercury line λ 2534·8, L.B.C. and T.B.C. are respectively components due to longitudinal and transverse sound waves. (*a*), (*b*) and (*c*) correspond to three different settings of the plate of diamond.

Fig. 12. Scattering of light in diamond at different temperatures.

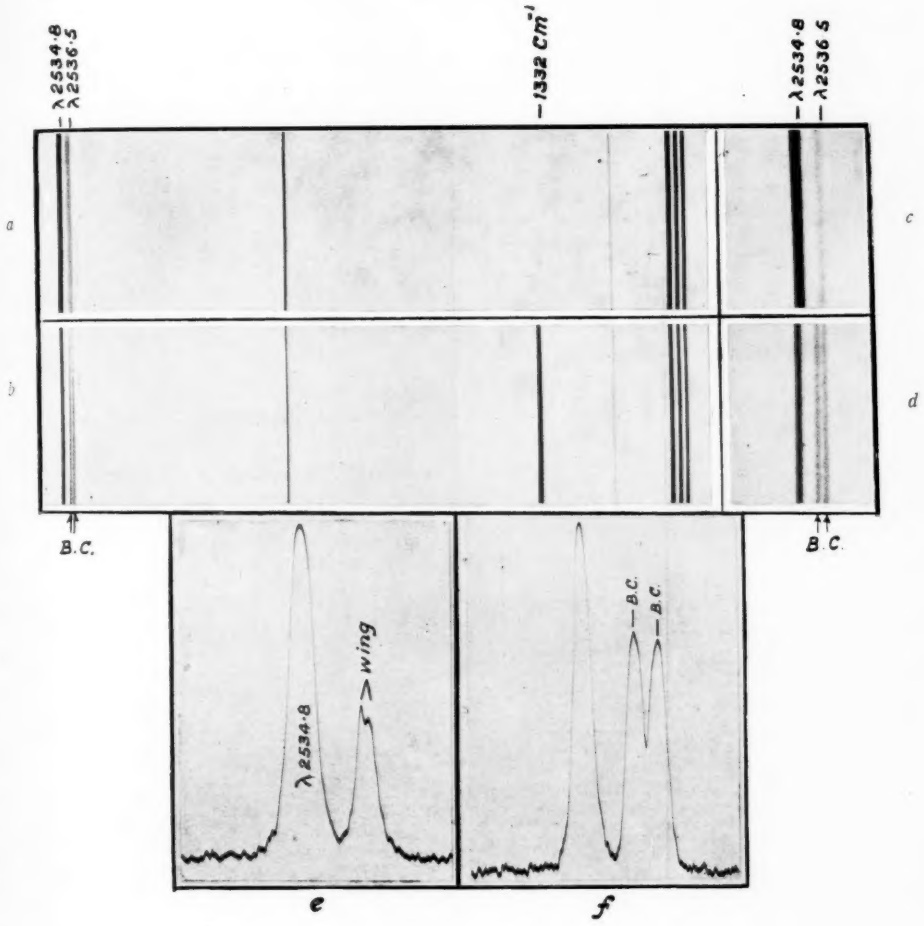

λ2534·8
λ2536·5
1332 cm⁻¹
λ2534·8
λ2536·5
a
b
c
d
B.C.
B.C.
λ2534·8
λ wing
B.C.
B.C.
e
f

FIG. 1

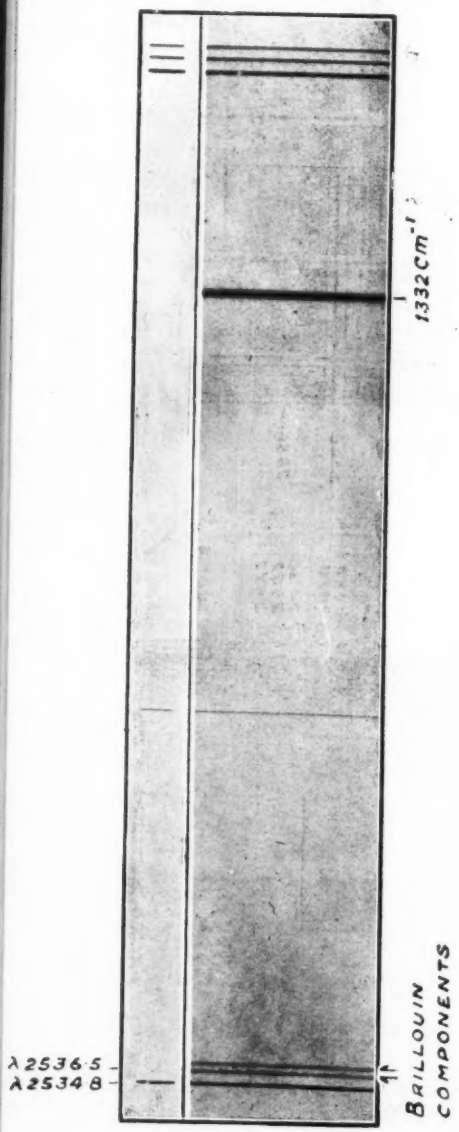
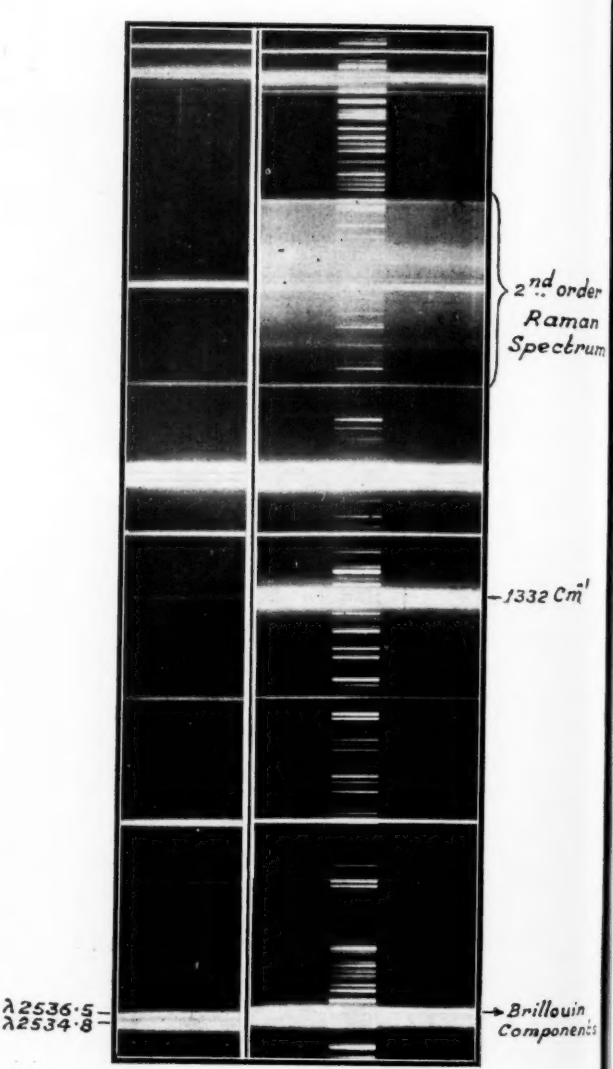


FIG. 6



a b

FIG. 2

FIG. 5

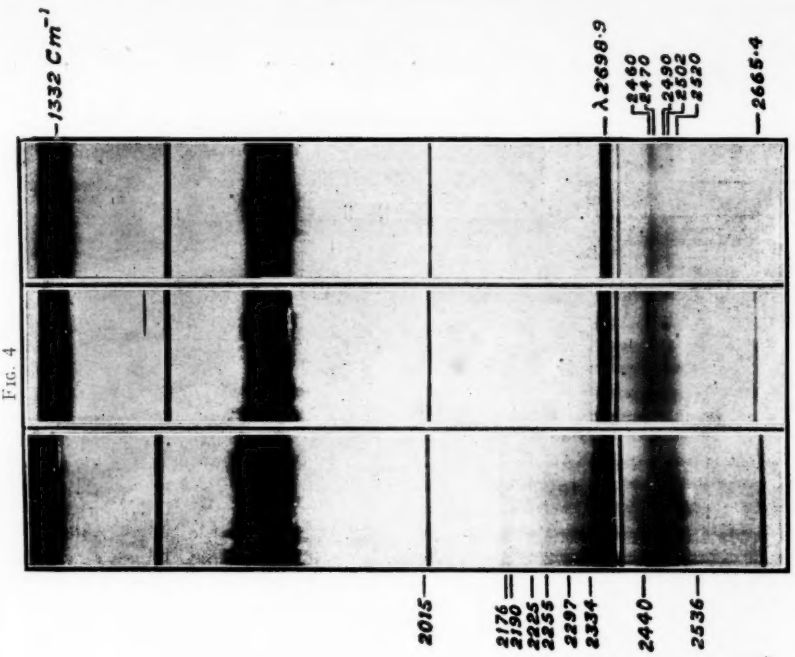

1332 Cm⁻¹
λ2698·9
2460
2470
2490
2502
2520
2665·4
a
b
c
2015
2176
2190
2225
2255
2297
2334
2440
2536

Fig. 4

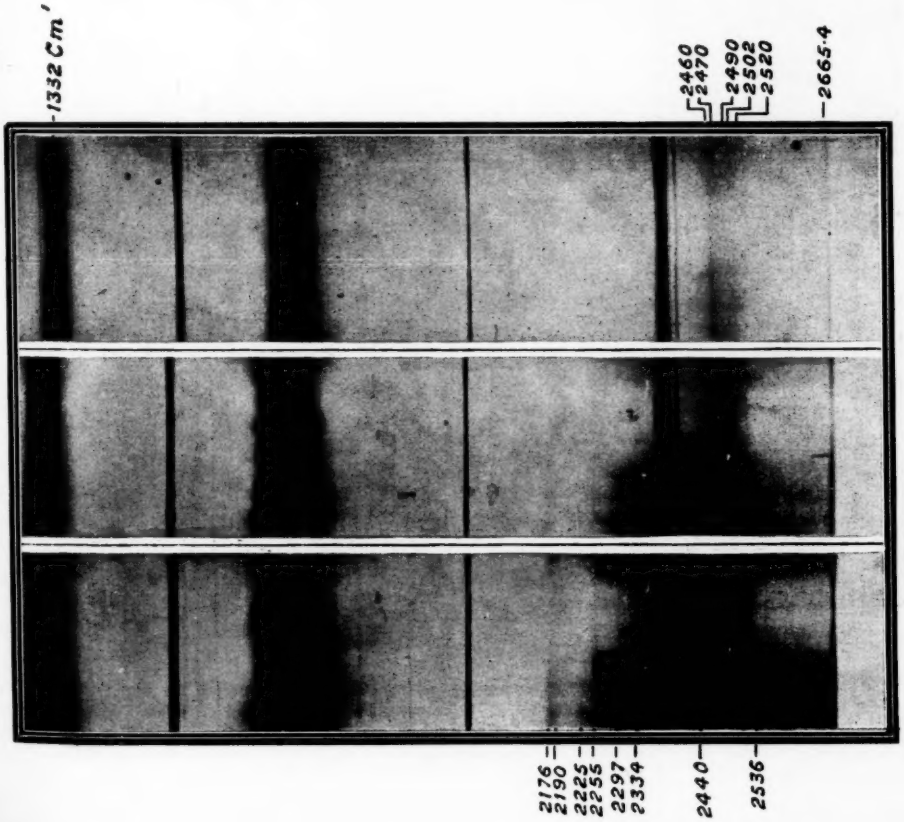

1332 Cm⁻¹
2460
2470
2490
2502
2520
2665·4
a
b
c
2176
2190
2225
2255
2297
2334
2440
2536

Fig. 5

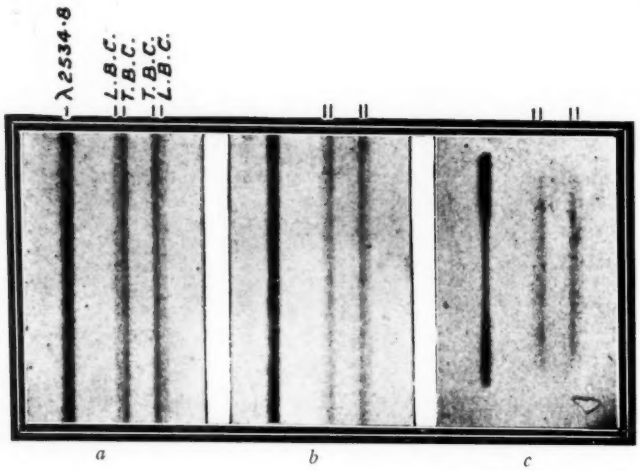

λ 2534·8
L.B.C.
T.B.C.
T.B.C.
L.B.C.
a
b
c

FIG. 7

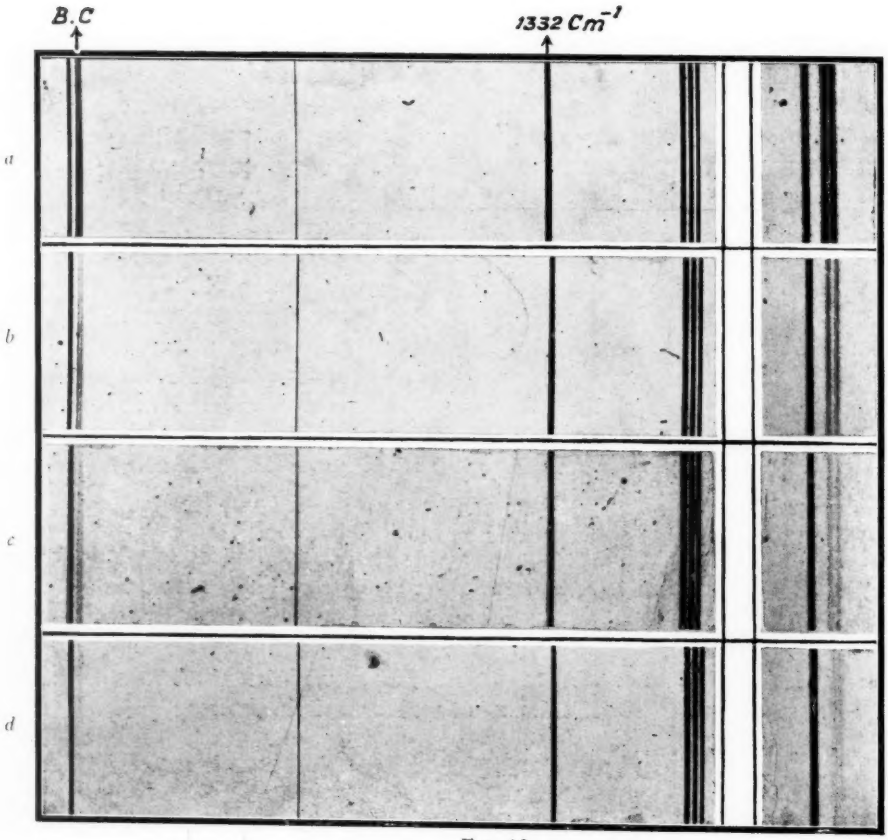

B.C
1332 Cm⁻¹
a
b
c
d
e 570°T
f 305°T
g 175°T
h 85°T

FIG. 12

THE RAMAN SPECTRUM OF ROCKSALT AND ITS INTERPRETATION

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1. Introduction

It is characteristic of crystals that their Raman spectra consist of discrete lines which are very sharp, particularly when recorded with the crystal held at a low temperature. The obvious and most natural interpretation of this fact is that the vibration spectra are themselves of that nature, in other words, that the regularly ordered three-dimensional structure of a crystal has a set of eigenvibrations with corresponding eigenfrequencies which are monochromatic. Basing himself on quite elementary and well-established dynamical principles, Sir C. V. Raman (1943) showed theoretically that this is the case and derived the result that a crystal with p atoms in a unit cell has $(24p-3)$ such eigenvibrations, and that the number of distinct eigenfrequencies would be further reduced if the crystal has other symmetries besides the three simple translations. The experimental confirmation of this proposition is obviously a matter of fundamental importance for the progress of crystal physics, and the cases that naturally suggest themselves as suitable material for a thorough investigation are those in which p is as small as possible, *e.g.*, diamond and rocksalt, where $p=2$.

According to the theory, the number of distinct eigenfrequencies for rocksalt is nine. Whereas in diamond one of the eigenfrequencies is active and gives a sharp and intense line as the first-order Raman spectrum, in rocksalt all the nine are inactive, and the study has therefore to be based solely on the second-order spectrum consisting of 9 octaves and 36 combinations of the primary vibrational frequencies. If all the 45 lines thus theoretically possible appeared in the spectrum with approximately equal intensities and were distributed uniformly over the narrow range of frequencies, and if their inevitable thermal broadening were also taken into consideration, the resulting spectrum could easily be mistaken for a continuous one, and it would have been a hopeless task to derive any useful results from its study. Fortunately, however, neither such equality of intensities nor such uniformity of distribution of frequencies is to be expected theoretically. The possibility is thereby opened up, by the use of refined spectroscopic technique, of

analysing the spectrum into its constituent lines and thereby establishing its true nature. In undertaking such analysis, it would clearly be an advantage to know, not merely that there are 9 fundamental frequencies whose overtones and combinations may appear in the spectrum, but also to know what these frequencies are, and to have an idea of the relative intensities with which the various overtones could be expected to appear in the second-order spectrum. These necessary preliminaries have been furnished in two theoretical papers respectively by K. G. Ramanathan (1947) and by Sir C. V. Raman (1947), appearing in these *Proceedings*, and the interpretation of the experimental results on an assured basis has thereby been made possible.

The earliest attempts of various authors to record the Raman spectrum of rocksalt using the λ 4358 excitation of the mercury lamp were unsuccessful. Later, Rasetti (1931) using the λ 2536·5 radiation successfully recorded the second-order spectrum. The reproductions of the spectrogram and its microphotometer record appearing with the paper of Fermi and Rasetti (1931) showed just such a structure for the spectrum as would be expected if it were an unresolved aggregate of lines unequally distributed, some of them being more intense than the others. Accordingly, in an earlier paper (R. S. Krishnan, 1943) the present author ventured to suggest that Rasetti's spectrum could be explained as representing mainly the octaves of the nine fundamental frequencies of rocksalt. Since, however, Rasetti had not given any measurements, and also in the hope of obtaining a more clearly resolved spectrogram, the experimental work of Rasetti was repeated using an instrument of the same type but with a finer slit. The results (Krishnan, 1945; 1946 *a*, *b*) confirmed the suggestion made previously, the microphotometer records showing clearly the existence of a number of sharply defined lines. In particular, the most intense line with a frequency shift of 235 cm.$^{-1}$ stood out clearly, appearing quite as sharp and intense as one of the lines of the mercury spectrum and being recorded both as a positive and negative frequency shift. Subsequently also, the author succeeded in recording the rocksalt spectrum with the large Hilger quartz E1 spectrograph and the resulting spectrogram was reproduced with a note in *Nature* (Krishnan, 1947). Since then, several fresh spectrograms and microphotometer records have been obtained. It is the purpose of the present paper to present the results together with a critical discussion of their interpretation.

2. The Structure of the Spectrum

As is well-known, in order to obtain a correct idea of the structure of any spectrum, it is necessary to examine it with a spectrograph of suitable

dispersion and resolution. In the case of molecular spectra which usually consist of a very large number of closely spaced lines, it is a familiar experience that spectrograms taken with a smaller instrument exhibit a system of unresolved broad bands showing little or no structure, whereas when examined with bigger spectrographs having sufficient resolution, the closely spaced lines are recorded clearly resolved from one another, thereby exhibiting unambiguously the discrete character of the spectra. Let us consider the case of spectra which consist of a few bright lines far apart from each other and superposed on a background composed of a great many feebler lines which are very close together and thereby appear unresolved. If examined under a spectrograph of small dispersion, such a spectrum would appear continuous, and the presence of the brighter discrete lines could easily be overlooked as they would be overpowered by the continuum. On the other hand, if an instrument of high dispersion is employed, the background would be weakened relatively to the individual lines, and the latter would then appear more prominently in the spectrograms. It is well-known also, that in heavily exposed spectrograms the photographic contrasts are greatly diminished and the presence of discrete lines is therefore less easily observed. In such cases, in order to gauge correctly the structure of the spectrum, it is necessary to take weakly or moderately exposed spectrograms. It may also be pointed out that if a spectrum is truly continuous, in other words, if it does not contain any detail beyond the power of a smaller instrument, the use of a larger instrument would not bring out any new detail but would, on the other hand, make even such detail as is present less obvious to inspection.

The foregoing remarks are relevant in relation to the facts noticed in the Raman spectrum of rocksalt. Even the spectrograms taken with the Hilger medium quartz spectrograph exhibited the characteristic features of the spectrum quite clearly. A typical spectrogram is reproduced in Fig. 1 (*c*) in Plate (XIII) and its microphotometer record is reproduced below as Fig. 2 with the more prominent peaks marked with the respective frequency shifts. The sharpness of some of the peaks, especially 235 and 350 cm.$^{-1}$, is comparable to that of any mercury line, showing thereby that these peaks represent Raman lines with discrete frequency shifts. This conclusion is further supported by the fact that the intense lines with frequency shifts 235 and 350 cm.$^{-1}$ are more prominently visible on the anti-Stokes side of the microphotometer record owing to the lightly exposed nature of the spectrum in this region. They are also seen clearly as lines on the anti-Stokes side of the spectrogram and are so sharp that they may be mistaken for mercury lines.

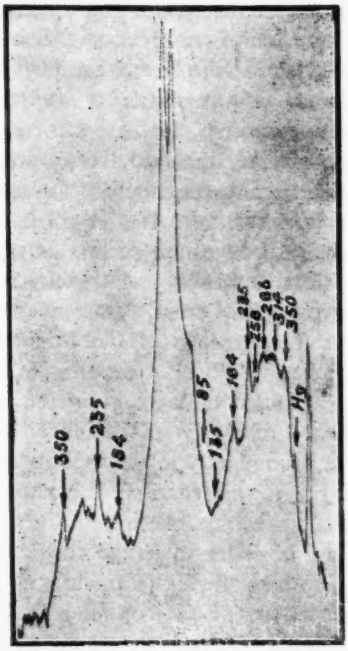

FIG. 2. Microphotometer record of the Raman spectrum of rock-salt taken with the medium quartz spectrograph.

A lightly exposed spectrogram of the Raman effect in rocksalt taken with the Hilger large quartz spectrograph is reproduced in Fig. 3 in Plate (XIV). Figs. 4 (*a*) and 4 (*b*) represent photographs enlarged to the same extent of the spectrograms taken with the large and medium quartz spectrographs respectively. A comparison of the two figures shows at once that the details of the spectrum are more clearly seen in Fig. 4 (*a*) evidently due to the higher dispersion and resolution of the larger spectrograph. A few salient features may be mentioned. The 235 line is definitely sharper and relatively more intense in the photograph taken with the larger instrument than in the other one. The doublet 343–50 cm.$^{-1}$ is seen more clearly separated from the rest of the spectrum in Fig. 4 (*a*) than in the other figure. The sharpness and the discrete character of the 235 line in particular become self-evident from a comparison of the microphotometer record of the spectrogram taken with the E1 spectrograph and reproduced in Fig. 5 below with that taken with the medium spectrograph and reproduced in Fig. 2. In the latter the line appears to be of the same intensity as some of the other prominent lines in the spectrum, whereas in the record shown in

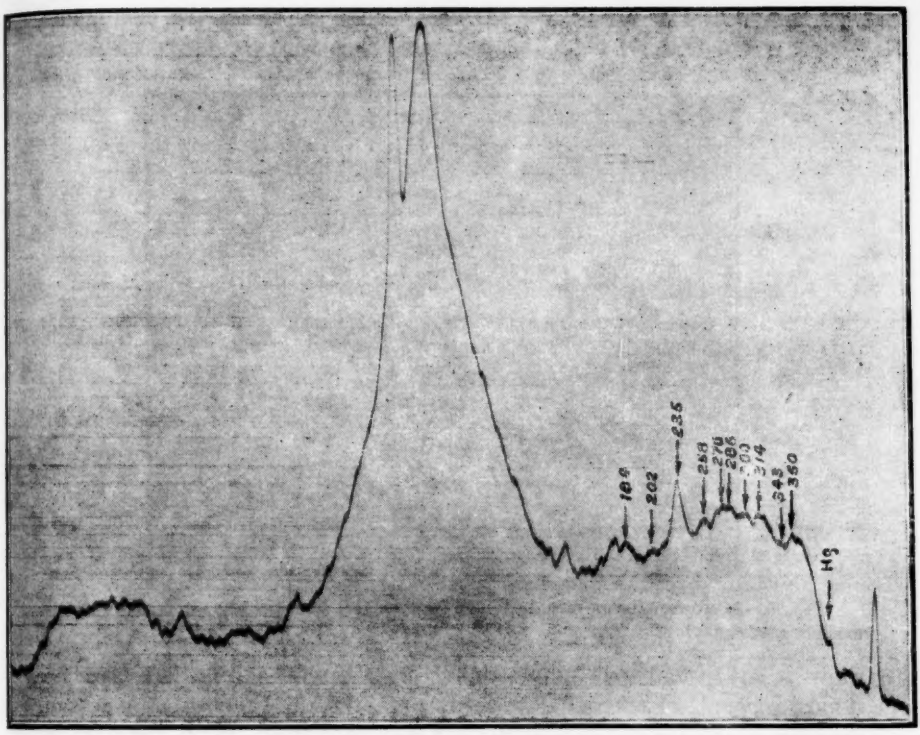

FIG. 5. The microphotometer record of the Raman spectrum of rocksalt taken with the E1 large quartz spectrograph.

Fig. 5, the line appears to be the most intense one. The explanation is obvious. Because of the better definition of the bigger instrument and the monochromatic character of the Raman line, the energy of the line is concentrated over a very small region in spite of the high dispersion, and in consequence the peak intensity of the line is enhanced relatively to some of the other lines which are not so sharp and fall in a region bunched up with lines.

From the above analysis, the structure of the Raman spectrum of rocksalt has been clearly established. The spectrum consists of a series of distinct Raman lines of which nine could be distinguished without difficulty in the photograph reproduced in Fig. 3. They are the prominent lines of the spectrum. There are three more lines with frequency shifts 202, 135 and 85 cm.$^{-1}$ which are comparatively feeble and are just discernible in the spectrogram taken with the medium spectrograph [see Fig. 1 (*c*)] in Plate (XIII). They are more clearly seen in the microphotometer record,

reproduced as Fig. 6. Besides the lines mentioned above, the microphotometer record (Fig. 5) of the spectrogram taken with the larger instrument

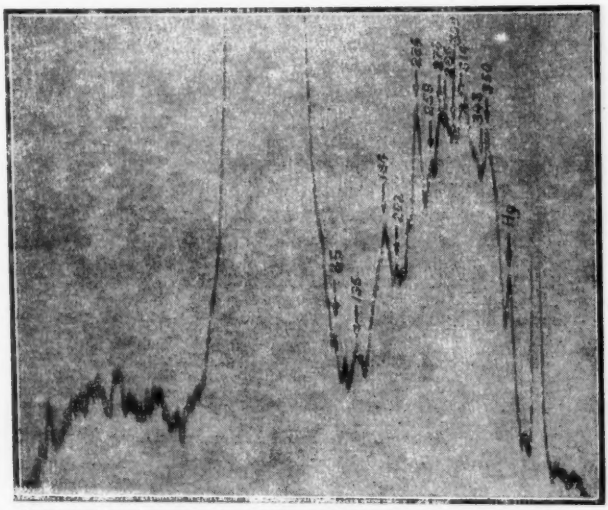

FIG. 6. Microphotometer record of the positive of the spectrogram taken with the medium spectrograph.

shows a large number of minor kinks. By a careful and critical examination of a couple of microphotometer records, the kinks due to graininess of the photographic plate were eliminated and only those which appeared in every record at the same place were taken into consideration. Table I gives the frequency shifts in wavenumbers from the exciting line of the Raman lines of rocksalt. the prominent ones being given in *italics*. Rough estimates of the relative intensities of the lines have also been made and their values are entered in Table I.

3. THE EXTENSION OF THE SPECTRUM

Rasetti had reported the existence of a low frequency band starting from zero frequency shift and extending up to about 60 cm.$^{-1}$ in the spectrum of rocksalt. Investigations carried out by the author definitely showed that there was no such band in the Raman spectrum. The band in this region appearing in the photograph taken by Rasetti is evidently due to optical coma in the instrument used by him. This fact will become evident from a comparison of the photographs reproduced in Fig. 1 in Plate (XIII). Figs. 1 (*a*) and 1 (*c*) are the photographs of the Raman spectrum of rocksalt taken with the E1 and medium quartz spectrographs respectively.

TABLE I

Second-order Spectrum

Sl. No.	Frequency shift in cm.$^{-1}$ observed	Relative intensity	Assignment
	Second-order Spectrum		
1	*85*	1	Octave $2\nu_9$
2	*135*	1	Octave $2\nu_8$
3	140	..	Combination $\nu_7+\nu_9$
4	162	..	Combination $\nu_6+\nu_9$
5	*184*	4	Combination $\nu_6+\nu_8$
6	199	..	Combination $\nu_5+\nu_8$
7	*202*	3	Octave $2\nu_7$
8	220	..	Combination $\nu_6+\nu_7$
9	*235*	10	Octave $2\nu_6$
10	*258*	6	Octave $2\nu_5$
11	270	..	Combination $\nu_4+\nu_5$
12	*276*	10	Combination $\nu_2+\nu_6$
13	*286*	10	Octave $2\nu_4$
14	*300*	8	Octave $2\nu_3$
15	*314*	9	Octave $2\nu_2$
16	320	..	Combination $\nu_1+\nu_4$
17	326	..	Combination $\nu_2+\nu_3$
18	*343*	7	Octave $2\nu_1$
19	*350*	8	
	Third-order Spectrum		
1	390	Very feeble	$2\nu_5$; $2\nu_6+\nu_2$
2	443	do	$2\nu_3+\nu_4$
3	459	do	$2\nu_2+\nu_4$; $2\nu_4+\nu_1$
4	475	do	$2\nu_3+\nu_1$; $3\nu_2$
5	507	do	$2\nu_1+\nu_2$

Figs. 1 (*b*) and (*d*) represent the spectra of the mercury arc taken with the same instruments. The coma is present in the bigger spectrograph also. The spurious band appears with the same intensity in the mercury spectrum.

On the higher frequency shift side, the rocksalt spectrum shows an abrupt fall in intensity after the 350 line. The photograph of the Raman spectrum does not indicate the presence of any band beyond this point. But the microphotometer record reproduced in Fig. 7 (*a*) below shows the existence of a weak tail extending up to about 520 cm.$^{-1}$ the intensity decreasing continuously with increasing frequency shift. The tail is not made up of a smooth curve but shows some structure. By critical examination of a couple of microphotometer records, it was possible for the author to identify the existence of at least five peaks with frequency shifts 390, 443, 459, 475 and 507 cm.$^{-1}$ These are included in Table II. The intensities of these are about 1/20th the intensities of the prominent lines in the main second-order spectrum. This observation is very significant. The feebleness of these

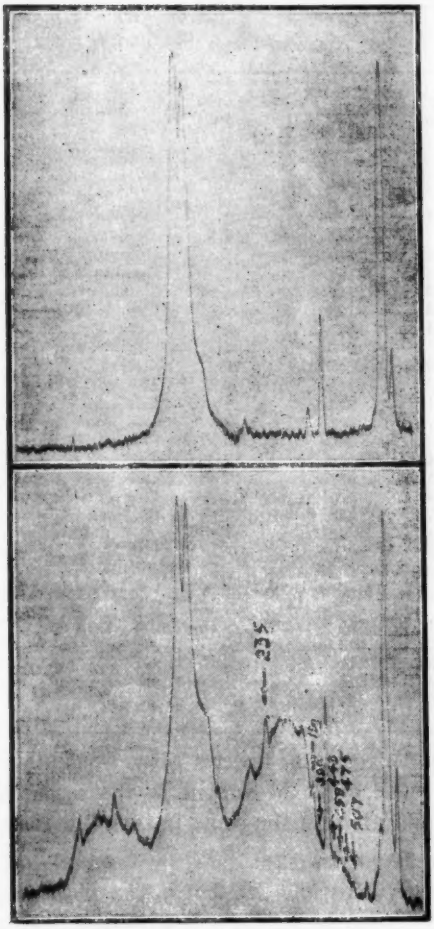

FIG. 7. (*a*) The microphotometer record of the Raman Spectrum of rocksalt taken with the medium quartz spectrograph. (*b*) The microphotometer record of the mercury spectrum.

lines and the magnitude of their frequency shifts indicate that they represent the third-order spectrum of rocksalt.

4. THE FUNDAMENTAL FREQUENCIES

In order to evaluate the fundamental frequencies using the expressions for the frequencies given by Ramanathan (1947) reproduced in Table II below, it is necessary to identify some of the second-order lines appearing in the Raman spectrum of rocksalt. Sir C. V. Raman (1947) has remarked

TABLE II

Sl. No.	Description of mode	Symbol	Degeneracy	Formula	Frequency in cm.$^{-1}$ calculated	Frequency cm.$^{-1}$ observed
I	Cubic planes oscillating normally, Na and Cl in same phase	ν_1	3	$\frac{P-8T}{m_1}+\frac{P'-8T'}{m_2}+\frac{16\,(T+T')}{m_1+m_2}$	173	175
II	Cubic planes oscillating tangentially, Na and Cl in opposite phases	ν_2	6	$\frac{P}{m_1}+\frac{P'}{m_2}+\frac{8(T+T')}{m_1+m_2}$	166	157
III	Na and Cl lattices vibrating against each other	ν_3	3	$\frac{P+8T}{m_1}+\frac{P'+8T'}{m_2}$	159	150
V	Octahedral Na planes vibrating normally	ν_4	4	$\frac{P-8T}{m_1}$	*143*	143
IV	Octahedral Na planes vibrating tangentially	ν_5	8	$\frac{P+4T}{m_1}$	*129*	129
VI	Octahedral Cl planes vibrating normally	ν_6	4	$\frac{P'-8T'}{m_2}$	*117*	117
VII	Octahedral Cl planes vibrating tangentially	ν_7	8	$\frac{P'+4T'}{m_2}$	104	101
VIII	Cubic planes vibrating normally, Na and Cl in opposite phases	ν_8	3	$-\frac{16\,(T+T')}{m_1+m_2}$	66	67
IX	Cubic planes vibrating tangentially, Na and Cl in same phase	ν_9	6	$-\frac{8\,(T+T')}{m_1+m_2}$	46	42

Note.—P and P′ represent the force on any atom proportional to its own displacement. T and T′ represent the force on any atom proportional to the displacement of the next nearest neighbours, force and displacement being along the same cubic axis and the plane containing the two being the cubic plane containing the two atoms. The undashed quantities refer to sodium ions and the dashed ones to chlorine ions. m_1 and m_2 are the respective masses of sodium and chlorine ions. $P \lessapprox P'$; $T \lessapprox T'$; $P \geqslant T$.

that because of the high refractivity of the chlorine ions, the oscillation of the chlorine layers against each other normally to the octahedral planes, *i.e.*, ν_6 in Table II, should appear with great intensity in the second-order spectrum. The 235 line is the most intense one and is therefore identified as the octave of ν_6. The normal oscillation of the corresponding layers of sodium ions, *i.e.*, ν_4 should also appear with a moderate intensity in the second-order spectrum. Moreover, the expressions for the frequencies are such that ν_4/ν_6 should be roughly equal to $\sqrt{m_2/m_1}$. The line with the

frequency shift 286 cm.$^{-1}$ satisfies the above relation. The tangential oscillations of the (111) sodium and chlorine layers (*i.e.*, ν_5 and ν_7) should only appear feebly in the second-order spectrum and their frequencies should also be roughly in the same ratio as ν_4 and ν_6. The lines 258 and 202 satisfy this relation. Therefore the lines 286, 258, 235 and 202 cm.$^{-1}$ can be identified as the octaves of ν_4, ν_5, ν_6 and ν_7 respectively. As will be evident from Table II, in order to evaluate the four constants P, P′, T and T′, it is enough if three frequencies are assumed, since there is a relation connecting the four force constants, namely $(P + 8T) = (P' + 8T')$. Accordingly, the frequencies of ν_4, ν_5 and ν_6 are taken as 143, 129 and 117 cm.$^{-1}$ respectively. The force constants have been evaluated.

$$P = 2{\cdot}43 \times 10^4 \text{ dynes/cm.}$$
$$P' = 2{\cdot}475 \times 10^4 \quad ,,$$
$$T = -0{\cdot}043 \times 10^4 \quad ,,$$
$$T' = -0{\cdot}049 \times 10^4 \quad ,,$$

Using the above values of the force-constants, the fundamental frequencies of all the modes have been evaluated and the results are shown in column 6 of Table II. Comparing the theoretical results with the frequency shifts of the prominent Raman lines listed in Table I, identification of the lines can be easily made. The lines with frequency shifts 350, 314, 300, 202, 135 and 85 are the octaves of ν_1, ν_2, ν_3, ν_7, ν_8 and ν_9 respectively. The fundamental frequencies calculated from the observed frequencies of the octaves are shown in column 7 of Table II. The agreement between the theoretical and observed values of the fundamental frequencies is fairly satisfactory. As is to be expected on theoretical grounds (Raman, 1947), the line 314 cm.$^{-1}$, *i.e.*, the octave of ν_2 is more intense than either the 300 line ($2\nu_3$) or the 350 line ($2\nu_1$), and the octaves of ν_8 and ν_9 are the weakest in the whole spectrum. The remaining lines listed in Table I can be satisfactorily explained as combinations and the respective assignments are given in the last column of Table I. The intensity of the 184 line is increased by the presence of a feeble mercury line falling adjacent to it. The intensity of the 276 line is also rather high for a combination. It is probable that because of its nearness to $2\nu_4$, its apparent intensity is enhanced. The line with the frequency shift of 343 cm.$^{-1}$ may be explained as arising from degeneracy splitting of the octaves of ν_1 or as due to a kind of Fermi resonance since the third harmonic of ν_6 falls on the top of the octave of ν_1. If one puts down all the 36 combinations which can appear in the second-order spectrum, no fewer than 20 of them are bunched together in the region of frequency shifts from 260 to 350 cm.$^{-1}$ This would account for the strong unresolved continuum appearing in this region of the observed spectrum.

The tail end of the spectrum to which reference has been made in the last section exhibits five lines which are satisfactorily explained as third-order combinations, and their tentative assignments are shown in column 4 of Table I.

Thus, in all its details, the spectroscopic behaviour of rocksalt as manifested in the Raman effect is fully and satisfactorily explained on the basis of the new theory of crystal dynamics put forward by Sir C. V. Raman.

6. Remarks on Born's Theory

Soon after the publication of the author's detailed paper on the Raman spectrum of rocksalt in the *Proceedings of the Royal Society*, a paper on the theory of the Raman effect in crystals by Born and Bradburn (1947) appeared in the same journal, in which these authors attempted to work out theoretically the Raman spectrum of rocksalt, and claimed that their results satisfactorily explained the facts as reported by Rasetti and by the author. This publication was received here only after sending the last communication to *Nature* (Krishnan, 1947) and therefore the author did not have any opportunity to reply to the remarks made therein. In subsequent communications to *Nature*, Born (1946, 1947) did not make any reference to the author's detailed paper, but persisted in the original claim of having satisfactorily explained the observed facts on the basis of his theory. The writer has carefully gone through the theoretical paper by Born and Bradburn and wishes to make the following comments.

For their theoretical calculations, Born and Bradburn have used the vibration spectrum of the rocksalt lattice as deduced by Kellermann on the basis of the Born-Karman theory of the cyclic lattice. The fundamental postulate of the latter theory is that all atomic vibrations can be considered as sets of waves traversing the crystal from end to end. The very appearance of the second-order spectrum is, however, inconsistent with this wave picture for two reasons. Firstly, it can be shown quite rigorously that if these waves extend over the entire volume of the crystal as postulated in the Born theory, the second-order effects in light-scattering from the individual cells of the lattice would cancel out by optical interference and therefore no Raman spectrum could be observed. This would be the case even if the waves are supposed to extend only to volume elements having the size of a few wavelengths of light. Secondly, the second-order effects, if any, are obtained by taking into consideration the anharmonicity arising from the finite amplitude of the atomic vibrations. These amplitudes should be a sensible fraction of the distance between Na and Cl ions, since otherwise the optical effects of anharmonicity would be quite negligible. The energy of any vibration

is $h\nu$ and that of its octave is $2h\nu$. If this energy is distributed over a very small number of atoms, as in the case of polyatomic molecules, the amplitude of vibration of every atom would be sufficiently large to give rise to second-order effects. If, on the other hand, each vibration is considered as a wave extending over the entire volume of the crystal or a volume element which is macroscopically small but large enough to include a great many lattice cells, the energy $2h\nu$ would be shared by an immense number of atoms, and the resulting amplitude of vibration would be too small to give any such effects of the second and higher orders. In the case of diamond, the observed intensity of the second-order spectrum is about 1/250th the intensity of the first order. In rocksalt, one does not observe any first-order spectrum but finds instead a second-order spectrum of appreciable intensity, and a weak third-order spectrum is also recorded. The very appearance of the higher order spectra indicates that as in the case of polyatomic molecules, the vibrations are localised, being restricted to the atoms in the individual cells of the lattice, or a very few of them. It follows therefore that the very basis of the theoretical calculations of Born and Bradburn is untenable.

Born and Bradburn admit that according to their theory the second-order Raman spectrum of rocksalt should be in the nature of a continuum exhibiting a few broad peaks. It is therefore not surprising that they misinterpret the observed spectrum as a continuous one with small superimposed peaks to suit their theory. Any one possessing a practical knowledge of spectroscopy would, however, have no difficulty in recognizing that the Raman shift of 235 cm.$^{-1}$ is actually a very sharp and comparatively intense line. Born and Bradburn have no explanation to offer for the appearance of this line, which even taken by itself, is a complete refutation of their theoretical ideas.

Born and Bradburn have given no explanation whatsoever for the activity or otherwise in the Raman effect of the various branches of combinational frequencies. They have arbitrarily chosen the coupling constants and the intensity factors in an attempt to fit the facts. In this process, they succeed in getting an intensity distribution curve which exhibits four broad peaks in the region of frequency shifts 200 to 370 cm.$^{-1}$ As will be evident from the microphotometer record reproduced in Fig. 5, of the present paper, apart from the extremely sharp line at 235 cm.$^{-1}$, the recorded spectrum exhibits no less than 18 observable peaks about the reality of which there can be no question, since they are perfectly reproducible. Their theoretical intensity distribution curve does not therefore resemble even remotely what has been recorded experimentally.

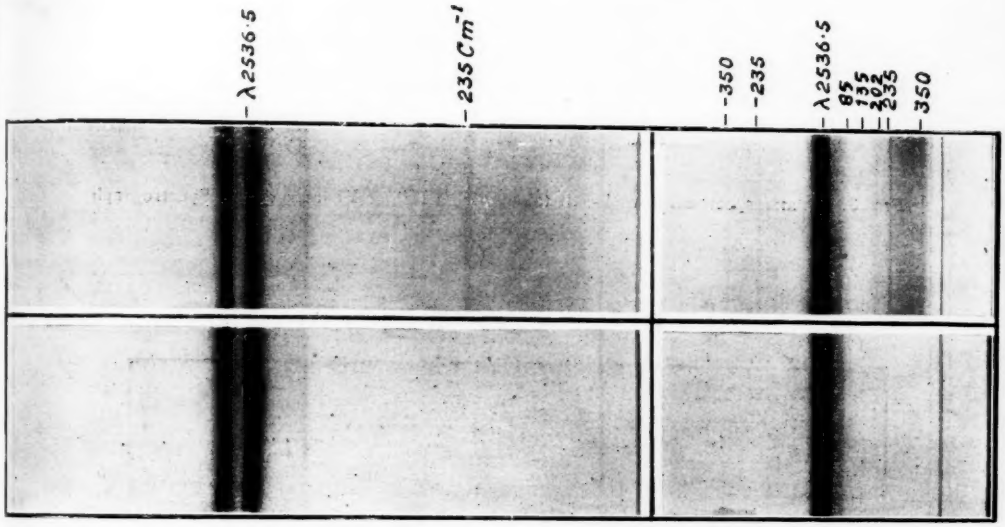

FIG. 1. (*a*) Raman spectrum of rock-salt taken with the large quartz Spectrograph
(*b*) Comparison Spectrum of the mercury arc
(*c*) Raman spectrum of rock-salt taken with the medium quartz Spectrograph
(*d*) Comparison mercury Spectrum taken with the same instrument

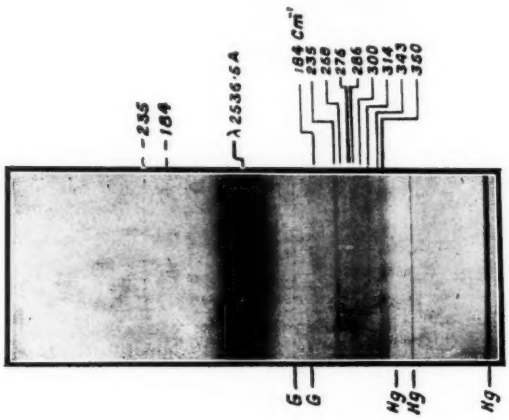

FIG. 3. Raman spectrum of rock-salt taken with a Hilger E1 large quartz Spectrograph

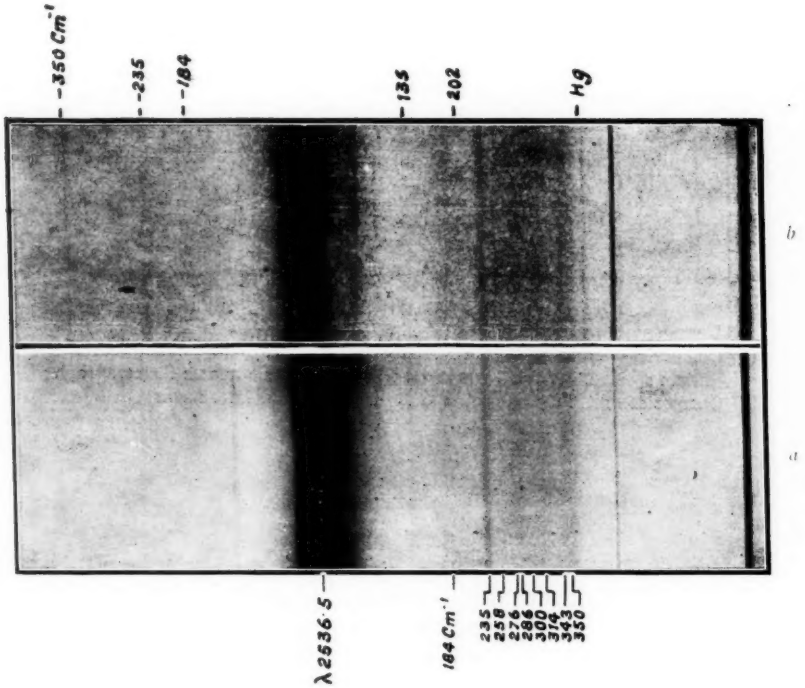

FIG. 4. Raman Spectrum of rock-salt (*a*) and (*b*) spectrograms taken with the large and medium quartz spectrographs respectively and enlarged to the same size.

Again, in trying to account for the broad band adjacent to the exciting line and extending up to 60 cm.$^{-1}$ reported by Fermi and Rasetti, Born and Bradburn have obtained two strong low frequency bands at 15 and 50 cm.$^{-1}$ which they ascribe to the activity of some differential branches of frequencies. The present investigation has, however, shown that there is no such band in the Raman spectrum, and that what has been reported by Fermi and Rasetti is patently due to optical coma in the instrument. If one proceeds on the basis adopted by Born and Bradburn, *viz.*, to adjust the theoretical calculations to fit the facts, one has necessarily to drop out their differential branches 12, 15, 17 and 18 which give rise to the low frequency bands, as they have no existence in the actual spectrum. Then one has necessarily also to drop out the corresponding summational branches, namely 6, 9 and 10. The theoretical curve would then be materially altered. This is only one illustration of the completely artificial character of the whole procedure adopted by Born and Bradburn.

The author is grateful to Prof. Sir C. V. Raman, F.R.S., for useful discussions.

7. Summary

By a careful microphotometric study of the spectrograms taken under high dispersion, it has been shown that the Raman spectrum of rocksalt consists of an aggregate of discrete lines some of which are more intense than the others. With the aid of the indications given by the theory regarding the vibration frequencies and their relative activities in light-scattering, nine of the more prominent lines in the spectrum have been identified as the octaves and the rest as combinations of the nine fundamental frequencies of oscillation of the rocksalt lattice. The views expressed by Born and Bradburn regarding the nature of the rocksalt spectrum and the explanations offered by them for its appearance have been examined and shown to be untenable.

References

Born, M. .. *Nature*, 1946, **157**, 810; 1947, **159**, 267.
—— and Bradburn, M. .. *Ibid.*, 1945, **156**, 567.
—— —— .. *Proc. Roy. Soc.*, A, 1947, **188**, 161.
Fermi and Rasetti, F. .. *Zeits. f. Physik.*, 1931, **71**, 689.
Krishnan, R. S. .. *Proc. Ind. Acad. Sci.*, A, 1943, **18**, 298.
———— .. *Nature*, 1945, **156**, 267; 1946 *a*, **157**, 623.
———— .. *Proc. Roy. Soc.*, A, 1946 *b*, **187**, 188.
———— .. *Nature*, 1947, **159**, 266.
Raman, C. V. .. *Proc. Ind. Acad. Sci.*, A, 1943, **18**, 237; 1947, **26**, 370.
Ramanathan, K. G. .. *Ibid.*, 1947, **26**, 493.
Rasetti, F. .. *Nature*, 1931, **127**, 626.

RAMAN SPECTRUM OF AMMONIUM CHLORIDE AND ITS VARIATION WITH TEMPERATURE

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1. Introduction

A study of the Raman spectrum of crystalline ammonium chloride and its variation with temperature is of great theoretical interest from two points of view. Firstly, as is well known, ammonium chloride crystal possesses a λ-point transition (=242·8° T.) at or in the vicinity of which its various physical properties exhibit anomalous behaviour. Pauling (1930) has suggested that the NH_4 ion is capable of free rotation above the transition temperature and the rotation changes to oscillation below that temperature and that the observed phenomena are just those expected to accompany the transition from rotation to oscillation of the NH_4 ion. Frenkel (1935), on the other hand, favoured the view that the NH_4 ion executed only torsional oscillations both above and below the transition temperature. A study of the Raman spectrum of ammonium chloride at different temperatures should throw some light on the behaviour of the NH_4 ion in the neighbourhood of the transition temperature.

Secondly, ammonium chloride crystallises in the cubic system, its structure being similar to that of cæsium chloride below 450° T. On the basis of the new crystal dynamics, a structure of the cæsium chloride type should have 11 fundamental frequencies of oscillation, none of which would be active as fundamentals in light-scattering. This would also be the case with ammonium chloride crystal if the NH_4 ion is capable of free rotation and in consequence possesses spherical symmetry. If, however, this condition be not satisfied because of the specific orientation of the tetrahedral NH_4 ion in the lattice, some of the 11 modes of oscillation in which the ion moves as a unit may be active as fundamentals in light-scattering. This actually proves to be the case, as we shall see and the study of the Raman spectrum of NH_4Cl, therefore, enables us directly to confirm the discrete nature of the vibration spectrum of the cæsium chloride structure.

2. Earlier Work

The Raman effect in ammonium chloride in the crystalline state has attracted a good deal of attention. The earlier investigators, namely,

Schæfer, Matossi and Aderhold (1930), Kastler (1932), Silveira, (1932), Holmes (1932) and Rao and Rao (1933, 1934) reported the existence of only a few lines in the spectrum of ammonium chloride. More detailed investigations were carried out by Menzies and Mills (1935), Holmes (1936) and Ananthakrishnan (1936, 1937). Menzies and Mills recorded spectrograms with the crystal powder maintained at the room temperature, $-24°$ C., $-28°$ C., $-32°$ C., $-65°$ C. and at $-150°$ C. respectively. The most interesting observation reported by them is the appearance of a lattice line with frequency shift 183 cm.$^{-1}$ when the temperature of the crystal is lowered below about $-30°$ C. For the NH_4 group, the same authors reported five diffuse lines at room temperature and seven sharp lines at $-150°$ C. Holmes worked with a single crystal of ammonium chloride and studied its Raman spectrum in the range from room temperature to well above 510° T. at which the crystal has the NaCl structure. Although he succeeded in recording the complete spectrum of the NH_4 group, *i.e.*, nine Raman lines, he failed to record any Raman line with a frequency shift less than 1400 cm.$^{-1}$ Employing the technique of complementary filters for crystal powders, Ananthakrishnan examined the Raman spectrum of ammonium chloride and confirmed the existence of eight of the nine NH_4 lines reported by Holmes. He also failed to record any low frequency line.

From what has been said above, it is clear that the results of the earlier workers on the Raman spectrum of ammonium chloride are incomplete, presumably because of the difficulty experienced by them in obtaining good photographs. Most of them used the λ 4046 and the λ 4358 radiations of the mercury arc as exciter. Single crystals of ammonium chloride being transparent to the ultra-violet, the use of the λ 2536·5 mercury resonance radiation as exciter suggests itself as a marked improvement in the technique of study, especially when one is interested in recording low frequency or lattice lines on a clear background. Accordingly, the author undertook a detailed investigation of the Raman spectrum of ammonium chloride in the form of a single crystal and its temperature variation, using the λ 2536·5 excitation.

3. Details of the Experiment

Single transparent crystals of ammonium chloride with well-developed faces were prepared by the method of slow evaporation from aqueous solutions of the salt to which a small quantity of urea was added.* The latter acts as a catalyst and facilitates the growth of the crystal. Kahlbaum's

* The author is indebted to Mr. K. G. Ramanathan who rendered assistance in the preparation of the crystals.

purest chemicals were used. The biggest grown crystal had the dimensions $2{\cdot}5 \times 2{\cdot}5 \times 1{\cdot}5$ cm. The specimens used in the present investigation were usually of the size $1 \times 1 \times 0{\cdot}5$ cm. Refractive index measurements were made with the ammonium chloride crystals. The measured value was the same as that of the pure salt indicating thereby that the crystals were not contaminated with urea. This conclusion was further supported by the fact that the Raman spectrum did not exhibit the characteristic urea lines even faintly.

The experimental technique employed for photographing the Raman spectrum using the λ 2536·5 excitation was the same as in the recent investigations of the author with various other crystals. For experiments below room temperature, a demountable Dewar flask was used. The crystal of ammonium chloride was firmly fixed to a copper block which was in turn screwed on to the lower end of the inner tube of the Dewar flask. The latter was provided with two quartz windows for illumination and observation. Liquid air, solid carbon dioxide in alcohol, solid carbon dioxide in acetone and salted ice were successively used as refrigerants. At very low temperatures the crystal acquired a fugitive yellow colouration on irradiation by ultra-violet light. For work above room temperature, a specially designed heater described in detail in one of the earlier papers of the author (Krishnan, 1946) was used.

A series of spectrograms was taken with the crystal held at seven different temperatures from 395° T. down to that of liquid air, *i.e.*, 85° T. A Hilger medium quartz spectrograph was used. With a slit-width of 0·04 mm., exposures of the order of 15 hours were given to get reasonably intense spectrograms at liquid-air temperature, whereas exposures of 3 hours sufficed for the room temperature photograph. Ilford special rapid plates were used. The negatives were measured with the aid of a Hilger cross-slide micrometer.

4. Results

Photographs of the Raman spectrum of ammonium chloride taken at 308° T. and 85° T. are reproduced in Figs. 1 (*b*) and 2 (*b*) respectively. The corresponding microphotometer records are shown in Figs. 1 (*c*) and 2 (*c*). Figs. 1 (*a*) and 2 (*a*) represent the spectrum of the mercury arc for purposes of comparison. The spectrograms taken by the author and reproduced in Figs. 1 and 2 exhibit many more Raman lines both in the low and high frequency shift regions than any recorded by the earlier workers. The positions and the frequency shifts of the Raman lines and bands are marked in the Figures. In order to get a very heavily exposed spectrogram at liquid-air temperature, crystalline quartz windows were used for the demountable

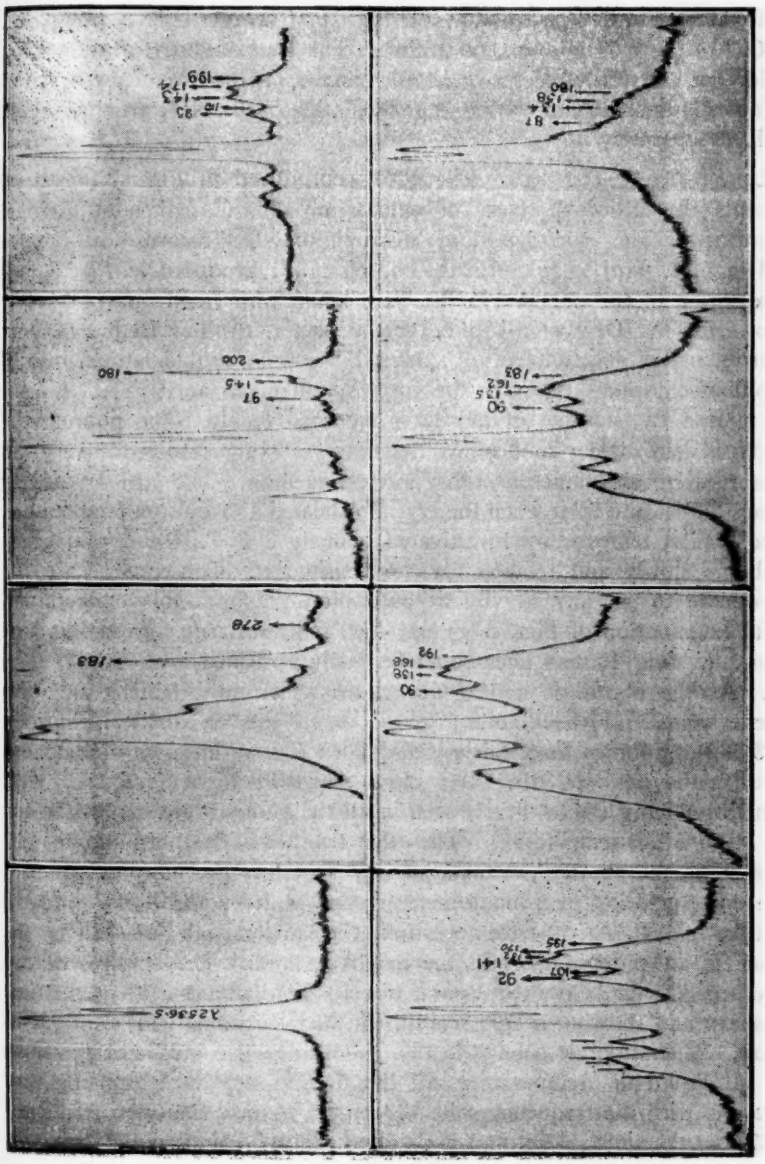

FIG. 4. (*a*) to (*g*) Microphotometer records of the lattice spectrum of ammonium chloride taken at different temperatures. (*h*) Microphotometer record of the mercury spectrum.

Dewar flask. With this arrangement some of the Raman lines of quartz appeared feebly in the spectrogram (see Fig. 2). The quartz lines are marked as "Q" in the microphotometer record. The Raman shifts of ammonium chloride are classified under two heads, namely, (1) low frequency or lattice lines and (2) lines due to the internal oscillation of the NH_4 group, and are described separately.

Lattice lines.—The series of spectra reproduced in Figs. 3 (*a*) to (*g*) represents the lattice spectrum of ammonium chloride taken at different temperatures. The corresponding microphotometer records are reproduced in Figs. 4 (*a*) to (*g*). As the photographs reproduced in Fig. 3 with the exception of the one at 195° T., were taken with fused quartz discs as windows for the Dewar flask and for the heater, the low frequency lines appearing in the spectra are not quartz lines, but genuine lattice lines of ammonium chloride. Even in the spectrogram taken at 195° T., only the most intense Raman line of quartz is recorded feebly. The photographs reproduced here, while confirming Menzies and Mills' results for very low temperature, reveal numerous other interesting facts. The lattice spectrum becomes diffuse and faint when the crystal is heated above room temperature. At the highest temperature investigated, namely 395° T., the crystal began to sublime slowly and thereby became translucent. Consequently, it was not possible to get any heavily exposed photograph at this temperature. Careful examination of Figs. 3 (*g*) and 4 (*g*) indicates that even at this high temperature, four Raman lines could be easily identified in the lattice spectrum. As the crystal is cooled down, the spectrum brightens and also sharpens considerably, exhibiting even above the so-called λ-transition (242·8° T.) a group of three fairly well-defined Raman lines with indications of three fainter ones. Of the latter, the one with the highest frequency shift is rather broad and can be clearly seen in all the photographs except the one taken at liquid-air temperature. The other two are fairly sharp and are just discernible in the photograph taken at 268° T. They are more clearly seen in the corresponding microphotometer record both on the Stokes and the anti-Stokes sides. At other temperatures they are partially masked by the presence of the intense lines in the neighbourhood. The features of the spectrum persist far below the λ-point transition, becoming at the same time quite sharp and showing progressive shift in their positions with falling temperature. A remarkable change in their intensities also occurs at the same time. At liquid-air temperature, all the lines disappear except the very intense one with the frequency shift 183 cm.$^{-1}$ A new line with frequency shift 278 cm.$^{-1}$ unmistakably makes its appearance. This is quite sharp but faint. See Figs. 3 (*a*) and 4 (*a*). The microphotometer record reproduced

in Fig. 2 (*c*) exhibits another faint line with a frequency shift of 91 cm.$^{-1}$ which is not one of the characteristic lines of quartz. In Fig. 4 (*a*) the existence of this line is not so clearly discernible as in Fig. 2 (*a*), probably due to the overexposure of the coma accompanying the exciting line. The frequency shifts of the lattice lines at different temperatures are entered in Table I. The photograph taken at room temperature shows the existence

TABLE I

Lattice Spectrum of NH_4Cl

Temperature °T	Frequency shifts in wave numbers							
85	91					183		278
173		97		145		180	200	
195		95	110	143		174	199	
268		92	107	141	152	170	195	
308		90		138		168	192	
348		90		135		162	183	
395		87		134		158	180	
Assignment	$2\nu_7$	ν_6	ν_5	ν_4	ν_3	ν_2	ν_1	$2\nu_4$

of a weak continuum starting from about 200 cm.$^{-1}$ and extending up to 380 cm.$^{-1}$ at which the intensity drops down to almost nothing.

The spectrum of the NH_4 group.—All the Raman lines with frequency shifts greater than 1400 cm.$^{-1}$ have been attributed to the internal oscillations of the NH_4 group. The spectrum at room temperature exhibits no less than 14 Raman shifts, some of which are sharp, some broad and the rest broad and diffuse. In the spectrogram taken at liquid-air temperature, no less than 23 Raman shifts could be identified as due to the NH_4 group. The frequency shifts of these are entered in Table II. Rough estimates of the relative peak intensities have been made and the values are given in Table II along with the description of the lines: *b*, *d*, and *s* represent broad, diffuse and sharp. The values of the frequency shifts of ammonium chloride recorded earlier by Menzies and Mills (1935) at 123° T. (— 150° C.) and those obtained by Holmes (1936) and by Ananthakrishnan (1937) for room temperature are also included in Table II for purposes of comparison. Menzies and Mills' data are far from being complete, while Holmes and Ananthakrishnan recorded all the important lines of the NH_4 ion exhibited at room temperature.

The general nature of the change which the spectrum undergoes as the temperature is progressively lowered, is best described by stating the appearance of the lines themselves. The Raman shifts entered in Table II have

TABLE II

Raman Spectrum of the NH_4 Group in Ammonium Chloride

Group	Low Temperature			Room Temperature			
	Menzies and Mills (1935) 123°T	Author (1947) 85°T	Relative peak Intensity	Holmes (1936)	Ananthakrishnan (1937)	Author (1947)	Relative peak Intensity
IV	1403 1464	1401 1420	5s 10s	1407 unresolved doublet	1398 1424	1400 1418 1440	15s 10b 8b
II	1712 1770	1716 1790 1810	 15s 10b	1709 1768	1700 1750	1710 1765 1780	 8b
VII		2025 2075	8b 5b	2010	2009	2010	10d
V	2870	2829 2876	10b 8b	2824	2813	2828	20b
I	3043	3048 3072	50s 15s	3041	3040	3041	50b
III	3123	3121 3138 3162	30s 26s 28s	3146	3142	3146	35b
VI		3215 3235 3285 3310 3365 3395 3420 3515 3535	10b 10b 6b 4b 2b 2b 1b 1d 1d	3232 3300		3231 3308 3380 3518	20b 15b 8b 2d

been classified into seven groups. The most intense Raman line appearing in the spectrum at room temperature has the frequency shift of 3041 cm.$^{-1}$ (Group I) and is rather broad. At liquid-air temperature this line becomes sharp and is followed by a feeble companion with a frequency shift of 3072 cm.$^{-1}$ The two lines with frequency shifts lying between 1700 and 1760 cm.$^{-1}$ which were reported by Holmes and Ananthakrishnan cannot be identified in the author's spectrogram as they fall on the top of the mercury triplet $\lambda 2652{\cdot}0$, $\lambda 2653{\cdot}7$ and $\lambda 2655{\cdot}1$. An examination of the spectrograms and the microphotometer record reproduced in Fig. 1 reveals that the outer components of the triplet which are separated from $\lambda 2536{\cdot}5$ by 1716 and 1760 cm.$^{-1}$, appear to have bulged out in the scattered spectrum due to the superposition of the Raman lines. Their frequency shifts have

therefore been tentatively taken as 1710 and 1765 cm.$^{-1}$ The room temperature photograph exhibits an additional broad line with a mean shift of 1780 cm.$^{-1}$ At liquid-air temperature, two lines with frequency shifts 1790 and 1810 cm.$^{-1}$ are seen clearly separated from the triplet. One Raman line with frequency shift 1716 cm.$^{-1}$ has been included in Table II. Its existence is inferred from the appearance of the mercury line λ 2652·0 on which it falls, and also from the fact that Menzies and Mills have reported a fairly intense line with a shift of 1712 cm.$^{-1}$ The intense and broad Raman line appearing in the spectrum at room temperature with a frequency shift of 3146 cm.$^{-1}$ splits up into a triplet with shifts 3121, 3138 and 3162 cm.$^{-1}$ at liquid-air temperature, the first one being the most intense. One of the three fairly sharp lines which appear at room temperature with shifts 1400, 1418 and 1440 cm.$^{-1}$, is absent in the spectrogram taken at liquid-air temperature. The relative intensities of the other two lines are reversed. Two broad bands lying at $\backsimeq$ 2010 and 2828 cm.$^{-1}$ in the spectrum at room temperature sharpen as the temperature is lowered. At liquid-air temperature each one of them has a companion band on the high frequency shift side. The photograph reproduced in Fig. 1 exhibits a group of four Raman bands with frequency shifts greater than 3200 cm.$^{-1}$, the intensity of the band decreasing with increasing frequency shift. Two bands $\backsimeq$ 3232 and 3300 cm.$^{-1}$ have already been reported by Holmes (1936). The four bands recorded in the present investigation split up into nine components with frequency shifts $\backsimeq$ 3215, 3235, 3285, 3310, 3365, 3395, 3420, 3515 and 3535 cm.$^{-1}$ when the temperature of the crystal is lowered to that of liquid air. These components may be seen only with some difficulty in the reproduced photograph, but they can be more easily identified in the microphotometer record (Fig. 2 *c*).

Besides the Raman shifts listed above, the spectrogram taken at room temperature exhibits four broad and diffuse bands 460–540, 670–780, 1065–1145 and 1280–1335 cm.$^{-1}$ respectively. They are marked as B_1, B_2, B_3 and B_4 in Fig. 1 (*a*). These bands cannot be attributed to the internal oscillations of the NH_4 ion. The intensity distribution in each band is asymmetrical, the low frequency shift end being more intense than the other. See Fig. 1. In the spectrogram taken at liquid-air temperature, one notices only two fairly sharp lines with frequency shifts 560 and 750 cm.$^{-1}$ See Fig. 2.

It should be remarked that as the temperature is lowered, the changes in relative intensity, width and number of the Raman shifts take place progressively. See the series of photographs of the complete spectrum of NH_4Cl reproduced in Fig. 5. The characteristic features of the liquid-air photograph begin to appear in the spectrum taken at 173° T. It will be seen from

the photographs (Fig. 5) that the intensity of the $\lambda 2536{\cdot}5$ line relative to that of its companion ($\lambda 2534{\cdot}8$) increases with increase in temperature. This can be explained as due to the fact that the unmodified scattered radiation is mostly made up of thermal scattering (Brillouin components) which is not absorbed by mercury vapour filter and whose intensity is directly proportional to the absolute temperature.

5. Discussion

Before discussing the significance of the results presented in the last section, it is useful to review the conclusions arrived at regarding the behaviour of the NH_4 ion from other investigations. It is known from X-ray studies (Bartlett and Langmuir, 1921; Wyckoff, 1922) that ammonium chloride possesses the cæsium chloride structure (body-centered cube); each nitrogen atom is surrounded by 4 hydrogen atoms tetrahedrally and by 8 chlorine atoms at the corners of a cube. Many physical properties of the crystal are found to vary sharply but continuously with temperature in the neighbourhood of the so-called λ-point transition ($242{\cdot}8°$ T.). As the temperature is raised through an interval of only a few degrees, the specific heat at constant pressure (Simon, 1922; and others, 1927; Ruhemann, 1927; Crenshaw and Ritter, 1932) and the coefficient of thermal expansion (Simon and Bergmann, 1930; Smits and MacGillavry, 1933; Adenstedt, 1936) increase many times in value and then decrease. Similar behaviour is also exhibited by the dielectric constant and dielectric absorption of ammonium chloride (Weigle, 1935). The crystal becomes strongly piezoelectric below the transition temperature (Hettich and Schleede, 1928; Hettich, 1934; Bahrs and Engl, 1937). From this observation Hettich concluded that the crystal has no centre of symmetry at low temperatures and therefore belongs to the class T_d, while at ordinary temperatures it belongs to the class O_h. X-ray studies carried out by Simon and von Simson (1926), Smits and MacGillavry (1933) and Ketelaar (1934) showed that the crystal structure remained unaffected as the temperature was lowered below the λ-point. The transition temperature is accompanied by a small volume change less than 1%. These investigators therefore concluded that the transition point should be associated in some manner with the behaviour of the hydrogen tetrahedra, since the light hydrogen atoms alone would not give any trace of their presence in the X-ray method.

In order to explain the observed anomalous behaviour exhibited by ammonium chloride crystal, Pauling (1930) put forward the hypothesis that at temperatures above the transition point, there would be free rotation of the NH_4 ion in the lattice. The failure to observe any lattice lines in the

Raman spectrum of ammonium chloride above the λ-point by Menzies and Mills (1935) is explained by them as due to the presence of free rotation of the NH_4 ion. Frenkel (1935), on the other hand, is opposed to the idea that free rotation starts just at the transition temperature, as there is no supporting evidence so far for the implied weakening of the interatomic binding force in the neighbourhood of the λ-point. He favours the view that both above and below the transition temperature, the NH_4 ion executes rotational oscillations. In the former case, there exists some order in the orientation of the axes about which oscillations occur, whereas above the transition temperature the orientations are irregularly distributed throughout the lattice. Lawson (1940) has calculated the temperature variation of the specific heat under constant volume from measurements on the temperature variations of adiabatic and isothermal Young's and rigidity moduli and the coefficient of thermal expansion, and has come to the conclusion that the transition is not associated with the occurrence of almost free rotation as suggested by Pauling. Lawson favours Frenkel's explanation, namely, that only a reorientation of the NH_4 ion takes place in the lattice at the transition temperature.

Let us now examine the spectroscopic behaviour of ammonium chloride in the light of what has been said above. The appearance of low frequency Raman lines constituting the lattice spectrum with great intensity in crystalline ammonium chloride at temperatures above the λ-point transition supports Frenkel's hypothesis rather than Pauling's. If the NH_4 ion is capable of free rotation and in consequence possesses spherical symmetry, none of the atomic vibrations of ammonium chloride in which NH_4 moves as a unit should appear as fundamentals in Raman effect due to the similarity of its structure to that of cæsium chloride. In fact, the Raman spectrum of ammonium chloride exhibits lattice lines with discrete frequency shifts even at as high a temperature as 395° T., showing thereby that the NH_4 ion is not capable of free rotation at this temperature.

At liquid-air temperature only one intense Raman line appears in the lattice spectrum with frequency shift 183 $cm.^{-1}$ which agrees with the rest-strahlen frequency of ammonium chloride (Rubens and Wartenberg, 1914). This line therefore represents the mutual oscillations of the NH_4 and Cl lattices against each other. The appearance of the fundamental vibration both in the scattering of light and in the infra-red absorption supports Hettich's suggestion that at very low temperatures the crystal does not possess any centre of symmetry and therefore belongs to T_d class. It follows therefore that there is a common preferred orientation for all the

hydrogen tetrahedra which have ceased to oscillate and are at rest in the crystal. Menzies and Mills (1935) are of the opinion that the orientations of hydrogen tetrahedra are such that a symmetry axis of the tetrahedron lies parallel to the diagonal axis of the cube. As the temperature is raised above 170° T., the full lattice spectrum of ammonium chloride makes its appearance in the Raman effect, indicating thereby that a definite change has taken place in the relative orientation of the hydrogen tetrahedra. The effect can be visualised as follows:—As the temperature is raised, the NH_4 ion begins to oscillate and the preferred orientation of the hydrogen tetrahedra gets disturbed. The slight mis-setting of the hydrogen tetrahedra during torsional oscillations makes all the lattice vibrations of the structure in which NH_4 moves as a unit, active in the Raman effect. This enables us to observe directly the discrete nature of the vibration spectrum of the cæsium chloride type of structure. As long as the torsional oscillations are of small amplitudes, the lattice lines should be sharp. As the temperature is still further increased, the oscillations become more violent and the orientations of the hydrogen tetrahedra tend to be more irregularly distributed resulting in a broadening of the lattice lines. This is what is observed experimentally. Thus, the spectroscopic data strongly indicate the correctness of Frenkel's picture regarding the behaviour of the NH_4 ion above and below the transition temperature.

Identification of the fundamental frequencies of the lattice.—The fact that the lattice spectrum of ammonium chloride consists of a finite number of discrete frequencies is a direct confirmation of the validity of the Raman dynamics. On the basis of the new dynamics, cæsium chloride structure has eleven fundamental modes of oscillation. They are enumerated in Table III for the case of the ammonium chloride structure. The expressions for the frequencies have been worked out by K. G. Ramanathan (1947) in a paper appearing elsewhere in these *Proceedings*. The approximate formula involving only four force-constants are given in column 5 of Table III. The frequencies of the 11 modes are in the descending order of magnitude. P and P′ represent the force on any atom proportional to its own displacement and T and T′ represent the force on any atom proportional to the displacement of the next nearest neighbours. The undashed quantities refer to the NH_4 ion and the dashed ones to Cl ion. m_1 and m_2 are the respective masses of NH_4 and Cl ions. To a first approximation the 11 modes have only 7 distinct frequencies, ν_1 to ν_7. Since $P \approx P'$ and $T \approx T'$, in order to evaluate the frequencies, we are justified in putting $P = P'$ and $T = T'$. If two of the lattice lines are identified, the remaining frequencies can be calculated using the formulæ given in Table III. The spectrum taken at

TABLE III

Vibration Spectrum of the NH_4Cl Lattice

Sl. No.	Oscillating planes	Nature and direction of Oscillation	Degeneracy	Formula $4\pi^2\nu^2C^2$		Frequency in cm.$^{-1}$ calculated	Frequency in cm.$^{-1}$ observed at 268°
I	Dodecahedral	NH_4, Cl in phase ; normally along $[1\bar{1}0]$ NH_4, Cl out of phase ; tangentially along [110]	6	$\frac{P-2T}{m_1}+\frac{P'-2T'}{m_2}+\frac{4(T+T')}{m_1+m_2}$	ν_1	179	195
II	Two Lattices	NH_4 against Cl, arbitrary	3	$\frac{P+2T}{m_1}+\frac{P'+2T'}{m_2}$	ν_2	170	170
III	Cubic	NH_4 alone oscillating normally along [100]	3	$\frac{P-2T}{m_1}$	ν_3	150	152
IV	Octahedral	NH_4 alone oscillating along any three orthogonal directions	3	$\frac{P-2T}{m_1}$			
V	Cubic	NH_4 alone oscillating tangentially along [010] or [001]	6	$\frac{P+2T}{m_1}$	ν_4	139	141
VI	Dodecahedral	NH_4 tangentially along [100] contained in the [110] plane	3	$\frac{P+2T}{m_1}$			
VII	Cubic	Cl alone oscillating along [100] normally	3	$\frac{P'-2T'}{m_2}$	ν_5	107	107
VIII	Octahedral	Cl alone oscillating in any three orthogonal directions	3	$\frac{P'-2T'}{m_2}$			
IX	Cubic	Cl alone oscillating tangentially along [010] or [001]	6	$\frac{P'+2T'}{m_2}$	ν_6	98	92
X	Dodecahedral	Cl tangentially along [100] contained in the [110] plane	3	$\frac{P'+2T'}{m_2}$			
XI	Dodecahedral	NH_4, Cl in phase; tangentially along [110] NH_4 Cl out of phase; normally along $[1\bar{1}0]$	6	$-\frac{4(T+T')}{m_1+m_2}$	ν_7	42	

268° T. exhibts the maximum number of lattice lines. From a comparative study of the figures given in Table I, it is seen that the mode in which the NH_4 and Cl lattices vibrate against each other has a frequency of 183 cm.$^{-1}$ at 85° T. which decreases to a value 170 cm.$^{-1}$ at 268° T. Therefore ν_2 can be taken as equal to 170 cm.$^{-1}$ The eleventh mode given in Table III should have a very low frequency. At 268° T. no line with frequency shift less than 90 cm.$^{-1}$ has been recorded. At liquid-air temperature two feeble lines with frequency shifts 91 and 278 cm.$^{-1}$ are recorded which should be assigned as octaves from intensity considerations. It is quite reasonable to assign the 91 line as the octave of ν_7. The corresponding fundamental will have a frequency of 45 cm.$^{-1}$ at 85° T. and 42 cm.$^{-1}$ at 268° T. Therefore ν_7 at 268° T. is taken as equal to 42 cm.$^{-1}$ Putting these values of ν_2 and ν_7 in the expression for frequencies, the values of P and T have been calculated:—

$$P = P' = 2{\cdot}176 \times 10^4 \text{ dynes/cm.}$$

$$T = T' = -0{\cdot}07 \times 10^4 \text{ dynes/cm.}$$

The force-constants in ammonium chloride are of the same order of magnitude as in sodium chloride. Taking the above values of the force-constants, the remaining five frequencies have been evaluated and are entered in column 7 of Table III. The measured values of the frequency shifts of the lines appearing in the spectrum at 268° T. are given in the last column of the same table. Considering the approximations made in the calculations, the agreement between the theoretical and observed values is satisfactory. It is important to point out that ν_2 is the most intense line below 180° T., while above that temperature ν_4 is the most intense one. The identification of the frequency shifts entered in Table I is shown in the last row of the same table.

The spectrum of the NH_4 ion.—Because of its tetrahedral symmetry, NH_4 ion in the free state should have only four distinct modes of oscillation of which ν_1 is single, ν_2 is doubly degenerate and ν_3 and ν_4 are triply degenerate. The corresponding Raman shifts are 3033, 1685, 3134 and 1397 cm.$^{-1}$ The observed frequency shifts in crystalline ammonium chloride lying in the neighbourhood of 3000, 1700, 3100 and 1400 cm.$^{-1}$ and classified under groups I, II, III and IV in Table II, represent the fundamental frequencies of internal oscillation of the NH_4 ion.

In the crystalline state the degeneracies of the frequencies of the free NH_4 ion appear to have been removed as indicated in Table IV. It will be evident from a comparative study of the figures given in this table that the degeneracy of ν_3 is removed only at very low temperature, *i.e.*, below 180° T. At liquid-air temperature only 8 lines due to the NH_4 ion are recorded. The

TABLE IV

Raman Frequencies of the NH_4 Ion

State	ν_1	ν_2	ν_3	ν_4
Free ..	3033	1685	3134	1397
NH_4Cl crystal at 308°T ..	3041	1710, 1765	3146	1400, 1418, 1440
,, at 85°T ..	3048	1716, 1790	3121, 3138, 3162	1401, 1420, ?

ninth one may be too feeble to be recorded. The appearance of nearly all the frequencies characteristic of a penta-atomic group in the spectrum of ammonium chloride suggests that in the crystal lattice the vibrating NH_4 ion possesses lower symmetry evidently due to the presence of potential fields of the neighbouring ions, although the NH_4 ion has the full tetrahedral symmetry when the atoms are at rest.

At liquid-air temperature, the intense Raman line with frequency shift 3048 cm.$^{-1}$ corresponding to the totally symmetric oscillation of the NH_4 ion has a weak companion at 3072 cm.$^{-1}$ The origin of this line and also of the band $\backsimeq$ 1780 cm.$^{-1}$ recorded at room temperature and the one $\backsimeq$ 1810 cm.$^{-1}$ at liquid-air temperature is not yet understood.

The spectrograms taken both at liquid-air temperature and at room temperature exhibit three groups of bands (V, VI and VII of Table II) with frequency shifts lying in the neighbourhood of 2800, 3200–3500 and 2000 cm.$^{-1}$ respectively, some of which are fairly intense. Holmes (1936) and Ananthakrishnan (1937) suggested that the band at $\backsimeq$ 2828 cm.$^{-1}$ might be the octave of the 1400 line. This suggestion is untenable since the 2828 band is more intense than the 1400 line. A comparison of the frequency shifts of the bands lying at $\backsimeq$ 2800 and 3200–3500 cm.$^{-1}$ with the characteristic frequency shifts of HCl and NH_3 observed in liquids and solutions shows that there is complete correspondence regarding the frequency shifts and relative intensity. It does not necessarily follow that there are free HCl and NH_3 molecules present in crystalline ammonium chloride at all temperatures. The significance of this result will, however, be discussed in a forthcoming paper by the author on the Raman spectrum of ammonium bromide and its temperature variation.

The reason for the appearance of a group of three diffuse bands between 450 and 1350 cm.$^{-1}$ in the spectrogram taken at room temperature and the line 560 cm.$^{-1}$ in the spectrogram at liquid-air temperature is at present not clear. The broad band 670–780 cm.$^{-1}$ (B_2) appearing at room temperature

and the sharp line at 760 cm.$^{-1}$ appearing at liquid-air temperature may be assigned as the intense 3041 band excited by λ 2399·4.

6. Infra-Red Spectrum

Infra-red absorption and reflection spectra of crystalline ammonium chloride have been studied by various workers, most of whom examined the 2–7 μ region. Rubens and Wartenberg (1914) were the only workers who studied the long wavelength region. They reported the existence of a strong reststrahlen frequency at 183 cm.$^{-1}$ corresponding to the principal oscillation of the ammonium chloride structure. Reinkober (1921) examined the infra-red spectrum of ammonium chloride by absorption and by reflection and recorded three maxima corresponding to some of the principal internal oscillations of the NH_4 ion. Hettner and Simon (1928) who investigated the influence of the transition temperature on the absorption of ammonium chloride in the 2–8 μ region, found that the absorption maxima at 1770 cm.$^{-1}$ in the warm chloride sharpened considerably and moved to 1800 cm.$^{-1}$ as the temperature was lowered. A similar behaviour is exhibited by the Raman lines at 1710 and 1765 cm.$^{-1}$ Wilberg (1930) subsequently reported the existence of nine absorption maxima with frequencies varying from 1400 to 3100 cm.$^{-1}$ Pohlmann (1932) has made a detailed investigation of the infra-red absorption spectrum of thin layers of ammonium chloride at room temperature and at $-$ 80° C. No less than 26 maxima at room temperature and 17 maxima at $-$ 80° C. could be identified from absorption curves reproduced by Pohlmann. These lie in the region of frequencies in wavenumbers from 1380 to 3385. The frequencies of the various maxima have been estimated and those which correspond to the observed Raman shifts are entered in Table V. Those which are shown in italics appear prominently in the Raman spectrum and in the infra-red absorption spectrum. It is interesting to note that the totally symmetric oscillation of the NH_4 ion which appears very strongly in the Raman effect is recorded only as a weak maximum in infra-red absorption. The activity of all the frequencies of internal oscillation both in Raman effect and in infra-red absorption indicates that the vibrating NH_4 ion has not the full tetrahedral symmetry. According to Pohlmann's data the 1400 and the 1700 cm.$^{-1}$ bands exhibit fine structure at room temperature which is absent at 193° T.

The fine structure in the 5–6 μ vibrational band of ammonium chloride appearing in the infra-red absorption has been resolved and studied in detail by Beck (1944). He recorded eleven peaks in the region 1608–1760 cm.$^{-1}$ with an average separation of 15 cm.$^{-1}$ between any two neighbouring peaks.

TABLE V

Low temperature		Room temperature	
Raman (Author) 85°T	Infra-red (Pohlmann) 193°T	Raman (Author)	Infra-red (Pohlmann)
3395	3400	3380	3385
3310	3335		
3285	3280		
3235	3247		
3131	*3146*	*3146*	*3160*
3072	3080		
3048	3025	*3041*	3065
2829	*2860*	*2828*	*2854*
1790	*1800*	1780	1804
		1765	*1777*
1716	1728	1710	1707
		1440	1443
1420	1426	1419	1426
1401	*1409*	*1400*	*1413*

The fine structure was attributed by Beck to the rotation of the NH_4 group in the molecule. The fine structure appeared practically unaltered at temperatures down to $-20°$ C. There was a change between $-20°$ C. and $-45°$ C. and the altered fine structure persisted down to at least $-60°$ C. The observed fine structure should be attributed to torsional oscillations of the NH_4 ion rather than to free rotation. As the Raman shifts lying in the $\backsimeq$ 1700 region fall on the intense mercury triplet in the spectrum taken with 2536·5 excitation, it has not been possible to confirm or deny the existence of the fine structure in Raman effect similar to the one reported by Beck in infra-red absorption.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest in the work.

7. SUMMARY

Using the λ 2536·5 mercury resonance radiation as exciter, the Raman spectrum of ammonium chloride has been investigated in detail over the range of temperature from 85° T. to 395° T. The recorded spectra at all temperatures exhibit many more frequency shifts than those obtained by the previous workers. The present study reveals the following facts:

(1) The Raman spectrum in the region of frequency shifts 90–200 cm.$^{-1}$ exhibits seven lattice lines, the frequency shifts and intensities of which show marked variations with temperature. These lines have been identified as the fundamental modes of vibration of the cæsium chloride structure, in

which the NH_4 ions oscillate as units, as demanded by the new crystal dynamics.

(2) The lattice spectrum persists far above the transition temperature. This fact indicates that Pauling's hypothesis that there is onset of free rotation of the NH_4 ions immediately above the transition temperature is not correct.

(3) The internal oscillations of the NH_4 ions exhibit nine distinct Raman shifts, showing thereby that these oscillations are not those of a freely vibrating tetrahedrally symmetric group.

(4) The spectra recorded at all temperatures reveal the presence of Raman shifts characteristic of HCl and NH_3 molecules.

References

1. Adenstedt, H. .. *Ann. d. Physik*, 1936, **26**, 69.
2. Ananthakrishnan, R. .. *Nature*, 1936. **138**, 803.
   ——— .. *Proc. Ind. Acad. Sci.* A, 1937, **5**, 76 & 175.
3. Bahrs, S., and Engl, J. .. *Zeit. f. Physik*, 1937, **105**, 470.
4. Bartlett and Langmuir .. *Journ. Amer. Chem. Soc.*, 1921, **43**, 84.
5. Beck, C. .. *Journ. Chem. Phys.*, 1944, **12**, 71.
6. Crenshaw and Ritter .. *Zeit. Phys. Chemie*, B, 1932, **16**, 143.
7. Frenkel, J. .. *Acta Physicochemica*, 1935, **3**, 23.
8. Hettich .. *Zeit. Phys. Chemie*, A, 1934, **168**, 353.
9. ——— and Schleede .. *Zeit. f. Physik*, 1928, **50**, 249.
10. Hettner and Simon .. *Zeit. Phys. Chemie*, B, 1928, **1**, 293.
11. Holmes, F. T. .. *Phys. Rev.*, 1932, **41**, 389.
    ——— .. *Journ. Chem. Phys.*, 1936, **4**, 88.
12. Kastler, A. .. *Bull. Soc. Chim. France*, 1932, **51**, 728.
13. Ketelaar .. *Nature*, 1934, **134**, 250.
14. Krishnan, R. S. .. *Proc. Ind. Acad. Sci.* A, 1946, **24**, 45.
15. Lawson .. *Phys. Rev.*, 1940, **57**, 417.
16. Menzies and Mills .. *Proc. Roy. Soc.* A, 1935, **148**, 407.
17. Pauling, L. .. *Phys. Rev.*, 1930, **36**, 430.
18. Pohlmann .. *Zeit. f. Physik*, 1932, **79**, 394.
19. Ramanathan, K. G. .. *Proc. Ind. Acad. Sci.* A, 1947, **26**, 500.
20. Rao, I. R., and Rao, C. S. .. *Cur. Sci.*, 1933, **2**, 209.
    —— —— .. *Zeit. f. Phys.*, 1934, **88**, 127.
21. Rubens and von Wartenberg .. *Ber. deuts. Chem. Ges.*, 1914, p. 69.
22. Reinkober, O. .. *Zeit. f. Physik*, 1920, **3**, 1; 1921, **5**, 192.
23. Ruhemann .. *Zeit. Phys. Chemie*, A, 1927, **129**, 339.
24. Schæfer, Matossi and Aderhold *Zeit. f. Physik*, 1930, **65**, 289.
25. Silveira .. *Comp. Rend.*, 1932, **195**, 521.

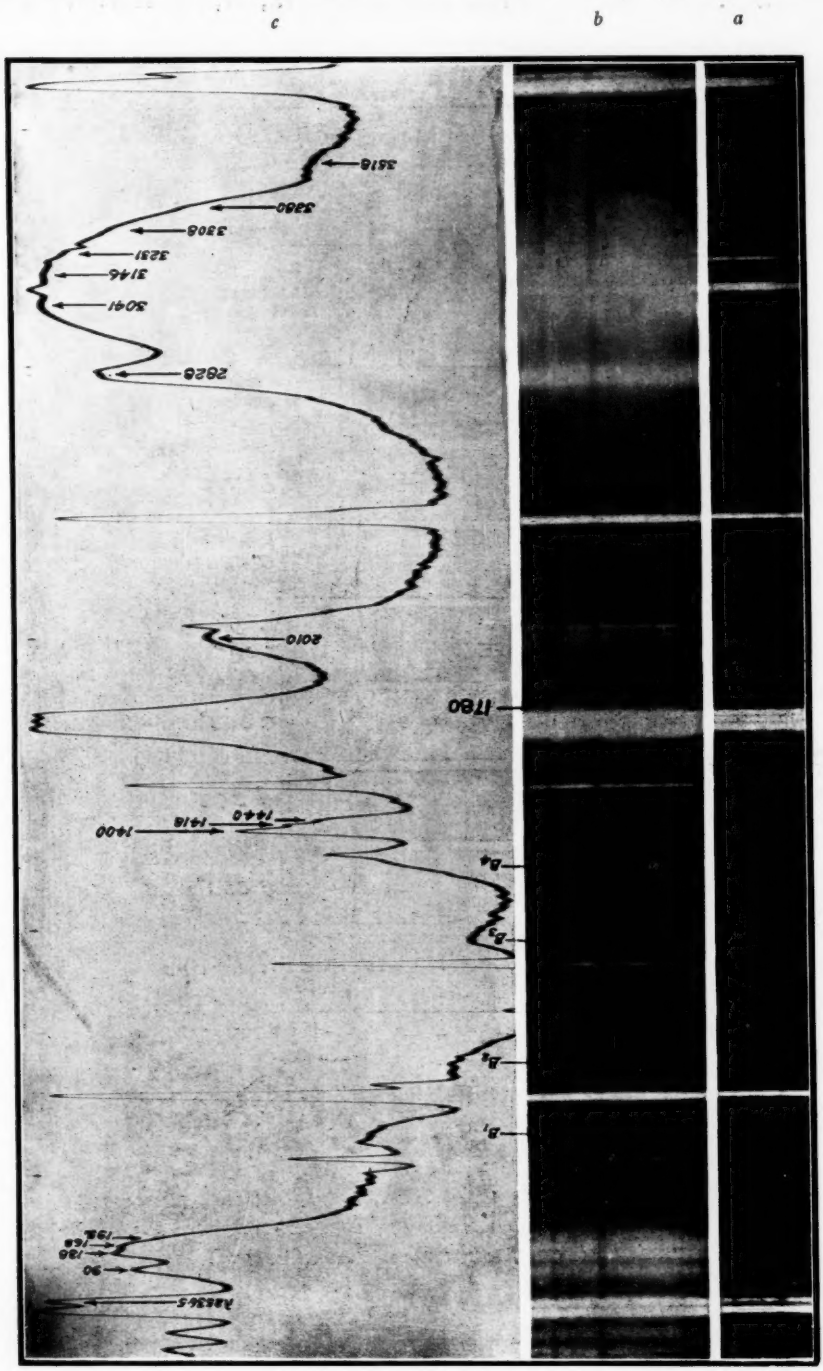
c
b
a
3518
3380
3308
3231
3146
3091
2826
2010
1780
1440
1418
1400
B4
B3
B2
B1
λ 8536.5
90
136
158
198

Fig. 1

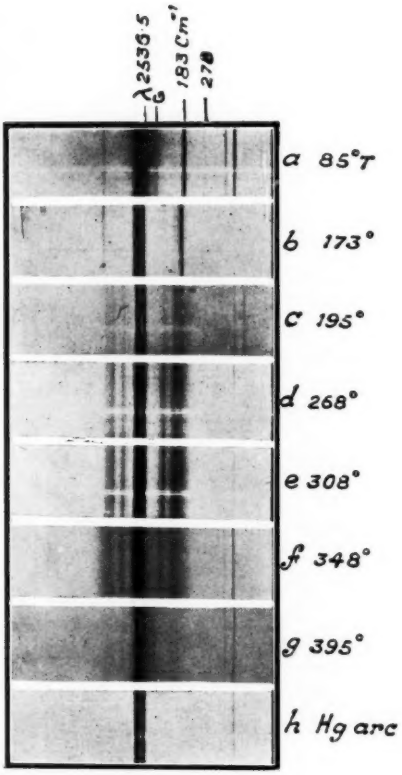

FIG. 3

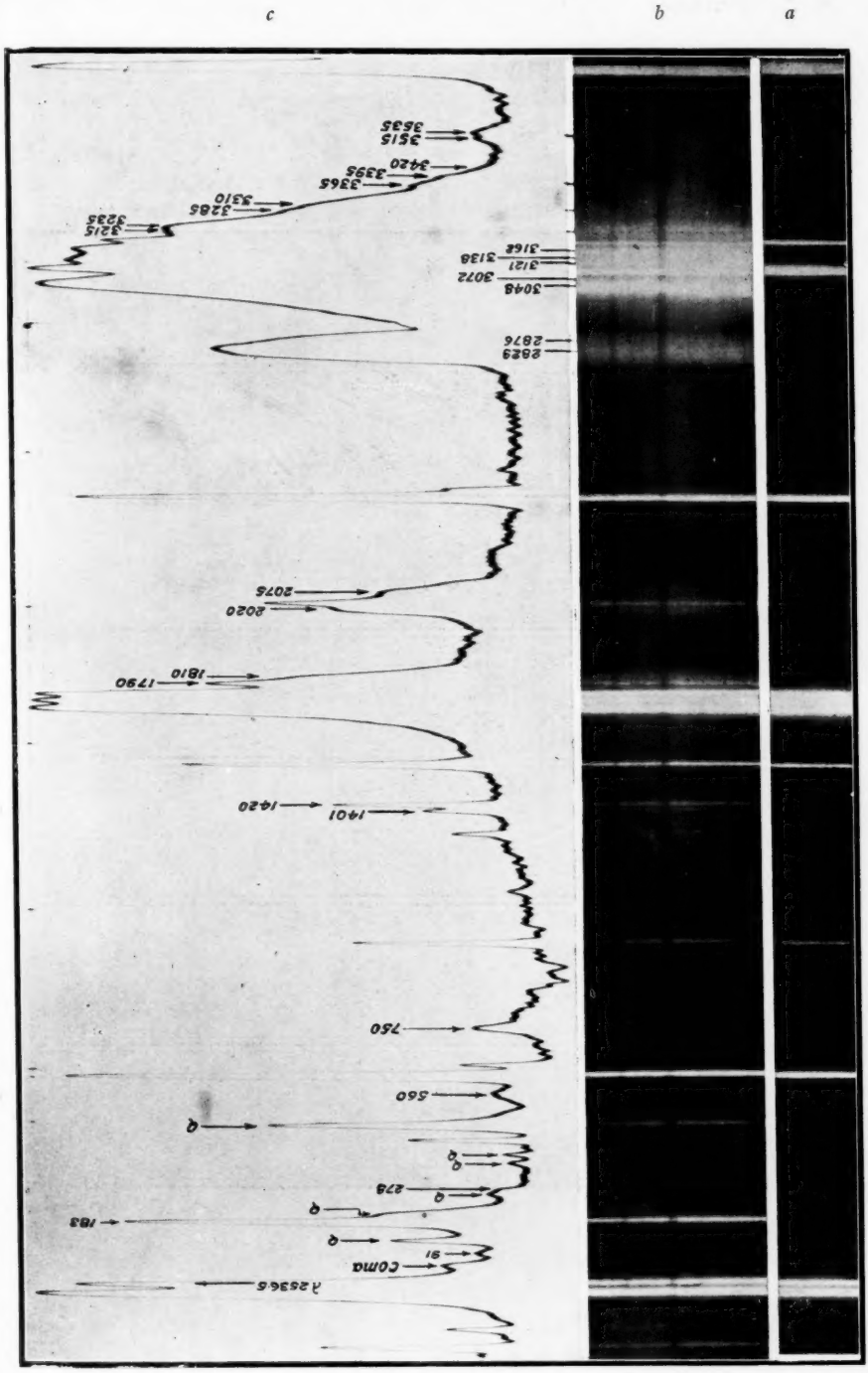
c
b
a
3635
3515
3420
3395
3365
3310
3285
3235
3215
3168
3138
3121
3072
3048
2876
2829
2076
2020
1810
1790
1420
1401
750
560
Q
Q
Q
Q
Q
278
183
91
COMA
λ2536.6

FIG. 2

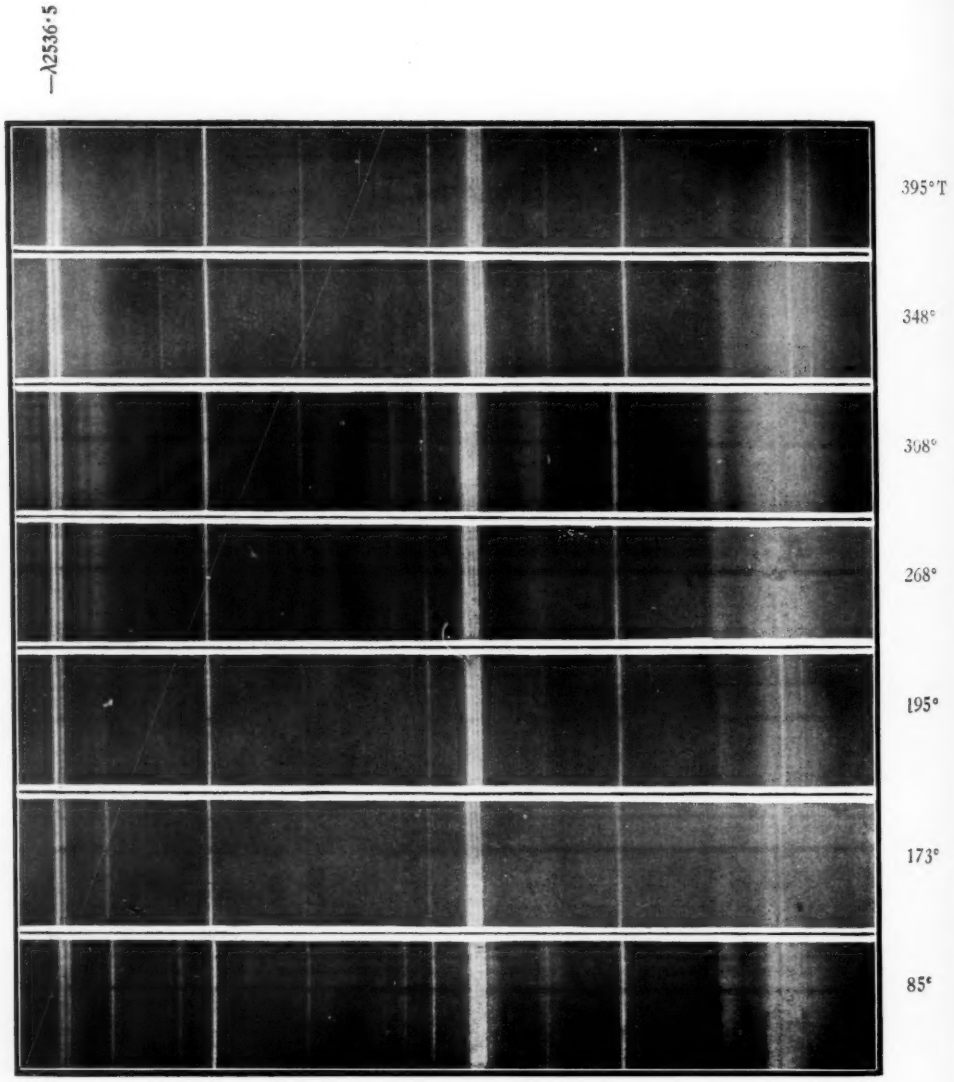

FIG. 5

26. Simon, F. .. *Ann. d. Physik*, 1922, **68**, 263.
27. ——— and von Simson, C. .. *Naturwiss.*, 1926, **38**, 880.
28. ——— — and Ruhemann, R... *Z. f. Phys. Chemie*, A, 1927, **129**, 339.
29. Simon, F. .. *Ber. deuts. Chem. Ges.*, 1926, **33**, 477.
30. Simon and Bergmann .. *Zeit. Phys. Chemie*, B, 1930, **8**, 255.
31. Smits and MacGillavry .. *Ibid.*, A, 1933, **166**, 97.
32. Weigle .. (1935) Referred to in Menzies and Mills' paper.
33. Wilberg, L. .. *Zeit. f. Physik*, 1930, **64**, 304.
34. Wyckoff .. *Amer. Journ. Sci.*, 1922, **3**, 177; **4**, 193.

Description of Plates

Plate XV

Fig. 1. (*a*) Spectrum of the mercury arc taken with a Hilger medium quartz spectrograph.
(*b*) Raman spectrum of ammonium chloride taken at 308° T.
(*c*) Its microphotometer record.

Plate XVI

Fig. 3. (*a*) to (*g*) Lattice spectrum of ammonium chloride.
(*h*) Comparison spectrum of the mercury arc.

Plate XVII

Fig. 2. (*a*) Spectrum of the mercury arc.
(*b*) Raman spectrum of ammonium chloride taken at 85° T.
(*c*) Its microphotometer record.

Plate XVIII

Fig. 5. Complete Raman spectrum of ammonium chloride taken with the medium quartz spectrograph.

RAMAN SPECTRUM OF ALUMINA AND THE LUMINESCENCE OF RUBY

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1. Introduction

A study of the Raman effect in alumina is of much theoretical interest as its vibration spectrum plays an important role in the luminescence and absorption spectra of minerals in which alumina forms the ground material. Hibben (1932) who was the first to examine the spectrum of alumina reported the existence of four weak Raman lines. However, the values of the frequency shifts given by him were not in agreement with those reported by the later investigators. In order to find an explanation for the numerous bands appearing in the luminescence and absorption spectra of ruby, Deutschbein (1932 *b*) photographed the Raman spectrum of alumina. He could observe only a single Raman line at 415 cm.$^{-1}$ Besides confirming the result of Deutschbein, Miss Mani (1942) reported the existence of an additional line at 376 cm.$^{-1}$ In a subsequent unpublished investigation, the same author recorded other faint lines in the spectrum of alumina besides the two already reported, among which two with frequency shifts 752 and 633 cm.$^{-1}$ appeared most definite. Both Deutschbein and Miss Mani employed the λ 4046 and λ 4358 radiations of the mercury arc for exciting the Raman spectrum of alumina which is comparatively very feeble. It is not surprising therefore to note that no spectrograms have been reproduced by these authors. Moreover, the results obtained by them are far from being complete, for, from group theoretical analysis, Bhagavantam has shown that alumina should have seven Raman active frequencies. In view of this, it appeared desirable to re-examine the Raman spectrum of alumina using a more powerful technique than the one employed by the earlier workers. A detailed study of the scattering of light and the Raman effect in alumina has therefore been made using the λ 2536·5 mercury resonance radiation as exciter, and valuable results have been obtained. A preliminary report of the same has appeared in *Nature* (Krishnan, 1947). Further details are presented in this paper together with a discussion of the significance of the results in relation to the luminescence spectrum of ruby.

2. Experimental Details and Results

While attempting to record the Raman spectrum of colourless synthetic alumina using the λ 2536·5 radiations, Roop Kishore (1942) found that the sample acquired a yellow colouration and became phosphorescent emitting a green radiation for a long time. The sample which was transparent to the 2536·5 radiations before the exposure, became practically opaque afterwards. Although the present writer confirmed the observations of Roop Kishore, it was found that certain specimens of synthetic alumina did not become coloured and opaque under ultra-violet irradiation. A large boule of synthetic alumina presented to Sir C. V. Raman by the Linde Air Products Co. of New York, belonged to this variety and was therefore chosen for the present study. It was in the form of a cylinder (6 cm. long and 2 cm. in diameter) with one end flat and polished and the other end tapered. The boule was clamped horizontally and was illuminated through the side. The scattered light emerging through the flat end was focussed on the slit of the spectrograph.

Doppler-shifted or Brillouin Components.—Fig. 1(*b*) represents the spectrogram of the scattered light taken with a Hilger large quartz (E1) spectrograph. A slit width of 0·04 mm. and an exposure of about 15 hours were used. Fig. 1 (*e*) represents the spectrogram of the incident radiation after quenching with a mercury vapour filter. The doubling of the 2536 line in the spectrum of the scattered light is clearly seen in Fig. 1 (*b*). The same effect is shown in the microphotometer record reproduced in Fig. 1 (*c*). The doubling is also clearly seen in the spectrogram taken with the medium quartz spectrograph and the microphotometer record reproduced in Fig. 1 (*d*) and (*a*). As is well-known, this doubling is due to a kind of Doppler effect arising from the selective reflection of the monochromatic light by the approaching and receding sound waves of thermal origin in alumina. The two components are termed as Doppler-shifted or Brillouin components. This is the first time that the existence of sound waves of thermal origin in alumina has been demonstrated experimentally. Because of the high value of the velocity of sound in alumina next only to diamond, it has been possible to record the Brillouin components directly using a quartz spectrograph of moderate power without any interferometric aid.

The frequency shifts of the Brillouin components from the exciting line have been estimated as well as their widths. The mean shift is $\pm$ 2·45 cm.$^{-1}$, while the width of each component is of the order of 1·8 cm.$^{-1}$ Taking the refractive index of alumina to be equal to 1·8, the velocity of sound waves responsible for the Doppler shift has been evaluated from the well-known

Brillouin formula. The value comes to about 7300 meters/sec. The angle of scattering was nearly 90° and the optic axis of the specimen lay in the plane of scattering equally inclined to the directions of incidence and observation. Therefore, the calculated value of the velocity is for sound waves travelling along the optic axis. As only one pair of broad Brillouin components is recorded, it is not possible to say whether the transverse and/or longitudinal sound waves were effective. Since the incident light had necessarily to be a convergent beam in order to shorten the time of exposure, there was a finite range for the angle of scattering θ round a mean value of 90°. Besides, the velocities of sound waves change with direction in the crystal. All these factors have tended to broaden the components and to mask their structure.

No direct determination of the sound velocities in alumina exists for comparison with the value obtained by the optical method. Even the measurements of the elastic constants of alumina are very scanty. Only the elastic constant along the optic axis has been determined. The order of magnitude of the sound velocity has therefore been computed from a knowledge of the density ρ and the elastic constant E_0 of alumina along the optic axis using the approximate formula $v_l = \sqrt{\frac{E_0}{\rho}}$ where v_l = velocity of longitudinal sound waves. Putting $E = 5 \times 10^{12}$ dynes/cm.^{2} and $\rho = 4$, the calculated value of the velocity is roughly 11,000 metres/sec. This is definitely higher than the value calculated from the mean shift of the Brillouin components. A possible explanation for this discrepancy is that each one of the Doppler shifted components is an unresolved combination of components arising from the longitudinal and transverse sound waves inside the medium and therefore the velocity calculated from the mean frequency shift should represent the mean of the velocities of the longitudinal and transverse sound waves. The value calculated from the elastic constant is for longitudinal sound waves.

It is interesting to compare the intensity of thermal scattering in alumina with that in diamond. For a depth of illumination equal to half a centimetre, the Brillouin components in diamond could be photographed with reasonable intensity in two minutes using the medium quartz spectrograph. In the case of alumina, on the other hand, for a depth of illumination of about 2 cm. in order to photograph the Brillouin components with the same intensity as in diamond, an exposure of two hours had to be given. This gives an idea about the extreme feebleness of the scattering in alumina. Unlike in diamond, the Brillouin components in alumina are more intense than the brightest Raman line (417 cm.$^{-1}$) of alumina (see Fig. 2 *a*).

Raman Spectrum.—The Raman spectrum of alumina taken with the medium quartz spectrograph and an exposure of one day is reproduced in Fig. 3 (*a*) together with a comparison spectrum of the mercury arc (Fig. 3*c*). The spectrum exhibits seven Raman lines. Their positions are indicated in the Figure along with the frequency shifts in wave numbers from the exciting line. The Raman lines are listed in Table I together with rough estimates of their relative intensities.

TABLE I

Raman Spectrum of Alumina

Serial No.	Frequency shift in cm.$^{-1}$	Relative intensity	Nature	Polarisation	Miss Mani (1942)
1	375	8	sharp	depolarised	376
2	417	10	sharp	depolarised	412
3	432	4	broad	depolarised	..
4	450	1	sharp	polarised	..
5	578	3	sharp	polarised	..
6	642	6	broad	depolarised	633
7	751	7	broad	polarised	752

The lines with frequency shifts 375, 417 and 642 cm.$^{-1}$ fall on or adjacent to the mercury lines $\lambda 2561{\cdot}2$, $\lambda 2563{\cdot}9$ and $\lambda 2578{\cdot}4$ respectively. But there is no difficulty in identifying them as two of them appear prominently on the anti-Stokes side, while the existence of the third is made certain by comparing the scattered spectrum with the spectrum of the direct arc. The Raman lines are clearly seen in the spectrogram taken with the large quartz E1 spectrograph and reproduced in Fig. 2 (*a*).

In order to determine the polarisation characteristics of the Raman lines for incident unpolarised light, a quartz double image prism with its axes horizontal and vertical and an ultra-violet transparent nicol with its principal plane inclined at angle of 45° to the vertical were interposed in the path of the scattered beam between the crystal of alumina and the condensing lens. The optic axis of the crystal was nearly parallel to the direction of observation. The resulting spectrogram is reproduced in Fig. 3 (*b*). The lines with frequency shifts 450, 578 and 751 appeared with greater intensity in the vertical component, indicating thereby that these lines are polarised, while the remaining ones are depolarised.

3. The Infra-Red Spectrum

Studies on the infra-red absorption and reflection spectra of alumina are very scanty. Coblentz (1908), who was the first to investigate the case, reported three maxima in selective reflection at $11\,\mu$, $11{\cdot}8\,\mu$ and $13{\cdot}5\,\mu$

corresponding to the frequency shifts of 909, 847 and 741 cm.$^{-1}$ Strong (1931) who investigated the reflectivity of alumina for specific wave-lengths in the region 20–150 μ, deduced three reflection maxima, a very strong one at about 23 μ (434 cm.$^{-1}$), a broad and less intense one between 27 μ and 29·5 μ and a very weak one at about 52 μ (192 cm.$^{-1}$). Recently, Parodi (1937), while examining the transmission of oxides in the far infra-red, reported the existence of three maxima of absorption in corundum at 30·5 μ (328 cm.$^{-1}$), 41 μ (244 cm.$^{-1}$) and 51·5 μ (194 cm.$^{-1}$). As reflections are generally observed on the shorter wavelength side of the corresponding absorption, it is reasonable to assume that the reflection peak between 27 μ and 29·5 μ reported by Strong and the absorption at 30·5 μ reported by Parodi are due to one and the same mode of oscillation of the lattice. Taking this into consideration, one observes in all six infra-red frequencies at 194, 244, 328–355, 434, 847 and 909 cm.$^{-1}$ The values are only approximate as some of them represent positions of reflection maxima. The reflection maximum at 13·5 μ (741 cm.$^{-1}$) may be assigned as the octave of 375 cm.$^{-1}$ A detailed study of the infra-red absorption spectrum of alumina using thin specimens is desirable.

4. Discussion of Results

The crystal structure of alumina is similar to that of calcite, the space group being D^6_{3d}. The unit cell is a rhombohedron containing two molecules. A group theoretical analysis of the normal modes of oscillation of the alumina lattice has been carried out by Bhagavantam and Venkatarayudu (1939). The main results are summarised in Table II.

Table II

P = permitted to appear; F = forbidden.

Class	No. of Modes	Raman	Infra-red	Observed frequencies in cm.$^{-1}$
A_1 ..	2	P	F	578, 751
A_2 ..	3	F	F	
B_1 ..	2	F	P	244, 847
B_2 ..	2	F	F	
E_1 ..	4	F	P	194, 328–355, 434, 909
E_2 ..	5	P	F	375, 417, 432, 450, 642

Of the 18 normal modes of oscillation with distinct frequencies, 7 are permitted to appear in Raman effect, 6 in infra-red absorption and the rest inactive in both. Consequently, there will not be any coincidence between the Raman and infra-red frequencies. Of the seven Raman-active frequencies, two come under the symmetric class and the rest under degenerate class. It is satisfactory to note that the Raman spectrum of alumina exhibits

seven frequency shifts in accord with the theoretical work of Bhagavantam and Venkatarayudu. Taking into consideration the state of polarisation and intensities of the Raman lines, the frequency shifts 578 and 751 cm.$^{-1}$ have been assigned to class A_1 and the rest to class E_2. Provisional assignments have also been made for the six infra-red frequencies. Further detailed assignment of the frequencies to the particular mode or modes contemplated by Bhagavantam and Venkatarayudu has not been made for two reasons. Firstly, data on the dependance of the Raman lines on the crystal orientation are lacking and secondly, the dynamics of the system has not been fully worked out.

5. Luminescence Spectrum of Ruby

The foreging results are of interest in relation to the luminescence and absorption spectra of ruby which, as is well-known, is crystalline alumina with chromic oxide impurity present as a colouring agent. Ruby is one of the most frequently examined substance in luminescence studies. The earliest investigations were those of du Fay (1724), Boisbaudran (1887), Crookes (1887, 1889), Miethe (1907), du Bois and Elias (1908), Becquerel (1907, 1910, 1911) and Mendenhall and Wood (1915). Recently, the subject has been studied by Deutschbein (1932 *a*, *b*, 1934), Venkateswaran (1935), Thosar (1938, 1941, 1942, 1944) and Miss Mani (1942). The investigations of Deutschbein and of Miss Mani were carried out with some thoroughness. As Deutschbein worked at liquid air temperature also, detailed reference is made here to the results reported by him. The emission and absorption spectra of ruby at 20° C. and − 195° C. are schematically represented in the accompanying chart (Fig. 4) which is taken from Deutschbein's (1932 *a*) paper.

The main features can be summarised as follows :—At room temperature, the luminescence spectrum consists of two sharp and intense lines λ 6927 and λ 6942 respectively, accompanied by other bands of varying width and intensity both on the longer and shorter wave-length sides of the principal doublet. These extend from λ 6583 to λ 7921. At liquid air temperature, the bands on the shorter wave-length side of the principal doublet disappear completely from the fluorescence spectrum. At low temperatures there is no correspondence between the fluorescence and absorption bands except in regard to the principal doublet and a few fairly sharp companion lines appearing on the longer wave-length side of the principal doublet and extending up to λ 7049.

It is now an accepted fact that the electronic transitions of the triply ionised chromium ions are responsible for the two principal intense lines

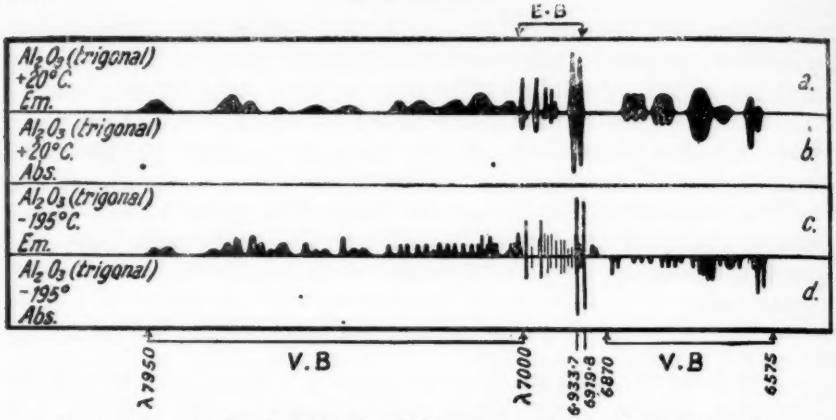

FIG. 4. Chart showing the emission and absorption spectra of ruby reproduced from Deutschbein's paper (1932).

V.B = vibrational bands, E.B = electronic bands.

at λ 6927 and λ 6942, as well as the fainter lines in the region λ 6927–7049 appearing at the same position in luminescence and absorption. Regarding the origin of the bands which lie on either side of the group of electronic bands (λ 6927–7049), Deutschbein was the first to suggest that these might arise from the combination of the vibration frequencies of the alumina lattice with the electronic transitions of Cr^{+++} ions. As he observed only one Raman shift (412 $cm.^{-1}$), he explained the fluorescence band at 7138 A.U. as due to this frequency. Miss Mani (1942), who reported four Raman lines, satisfactorily accounted for eight of the vibrational fluorescence bands on the Stokes and anti-Stokes sides of the principal doublet as due to the modulation of the electronic transitions by the crystal lattice vibrations. As the author has succeeded in recording the complete Raman spectrum of alumina, it is now possible to give more complete and satisfactory assignments for most of the vibrational bands of ruby than had been done by the earlier workers. Table III gives the list of all the vibrational bands observed by Deutschbein both in absorption and emission at — 195° C. The bands at λ 6596, λ 6680 and λ 6694 appearing in absorption spectrum have been omitted from the table as there are no corresponding bands in the luminescence spectrum.

On the basis of the seven Raman frequencies listed in Table I, 8 absorption bands on the anti-Stokes side of the principal doublet and 13 luminescence bands on the Stokes side have been quantitatively accounted for. The corresponding assignments are given in Table III. It is interesting to note that while the more intense principal line R_1 (λ 6933·7) of chromium is responsible for the majority of the vibrational bands, there are some bands

TABLE III

Vibrational Bands of Ruby appearing in Luminescence and Absorption Spectra at — 195° C.

Emission

Ser. No.	Wave length in A.U.	Wave number in cm.$^{-1}$	Intensity	Width	Shift in cm.$^{-1}$ from λ 6933·7, R_1	Shift in cm.$^{-1}$ from λ 6919·8, R_2	Assignments from lattice spectrum
			Absorption				
1	6574·5	15208	5	10		761	751 R
2	6586·1	15179	6	10	761		751 R
3	6620	15101	2	10	683		ν_9
4	6640	15056	2	45	638		642 R
5	6654	15025	2	10		578	578 R
6	6672	14984	4	8	566		578 R
7	6688	14948	3	8	530		ν_8
8	6707	14906	2	10	488		ν_7
9	6729	14858	1	10		411	417 R
10	6744	14825	2	10	407		417 R
11	6757	14796	2	10	378		377 R
12	6768	14771	2	10	353		ν_6
13	6790	14724	1	10	306		ν_5
14	6807	14686	1	10	268		ν_4
15	6823	14652	1	10	234		ν_3
16	6854	14586	2	8	168		ν_2
17	6866	14561	3	6	143		ν_1
	6919·8	14447	9	3		Principal line R_2	
	6933·7	14418	10	4		Principal line R_1	
			Emission				
1	7001·8	14278	4	3	140		ν_1
2	7012·5	14256	2	3	162		ν_2
3	7058·2	14164	3	5	254		ν_3
4	7067·4	14146	1	10	273		ν_4
5	7075·7	14129	1	10	289		$2\nu_1$
6	7082	14116	0	8	302		ν_5
7	7105·2	14070	1	7		377	375 R
8	7110·5	14060	1	7	358		ν_6
9	7120·0	14041	3	8	377		375 R
10	7124·3	14033	2	8		414	417 R
11	7131·6	14018	1	8		427	432 R
12	7139·6	14003	3	8	416		417 R
13	7145·9	13990	2	8	428		432 R
14	7161·3	13960	2	12	458		450 R
15	7178·1	13928	2	9	491		ν_7
16	7196	13893	2	10	525		ν_8
17	7211	13863	2	10		584	578 R
18	7231	13825	2	10	593		578 R
19	7245	13799	1	10		648	642 R
20	7260	13770	2	14	648		642 R
21	7279	13735	2	14	683		ν_9
22	7303	13689	2	12		758	751 R
23	7318	13661	2	14	757		751 R
24	7346	13609	2	14	809		ν_{10}
25	7404	13503	1	20	915		ν_{11}
26	7428	13458	1	20	960		375+578 R
27	7452	13415	3	10	1003		417+578 R
28	7494	13340	1	18		1107	
29	7514	13304	1	18	1114		
30	7538	13262	2	18	1156		2 × 578 R
31	7595	13163	2	50	1255		
32	7627	13108	1	20	1310		
33	7649	13070	1	18			
34	7669	13036	3	18	1382	1377	642+751 R
35	7709	12968	3	15	1450		
36	7739	12918	2	20	1500		2 × 751 R
37	7770	12866	1	40	1552		
38	7890	12670	1	60	1748		
39	7926	12613	1	60	1805		

R in column 8 represents that the particular frequency shift is observed in Raman spectrum.

which arise from the modulation of the less intense principal line R_2 (λ 6919·8). As is to be expected, the bands arising from the latter are less intense than those arising from the former. More or less perfect mirror image symmetry about the principal line R_1 (λ 6933·7) holds for the 9 bands λ 6866, 6854, 6823, 6807, 6790, 6768, 6707, 6688 and 6620 on the anti-Stokes side and for the bands λ 7001·8, 7012·5, 7058·2, 7067·4, 7082, 7100·5, 7178·1, 7196 and 7279 on the Stokes side. The corresponding vibrational frequencies are denoted by ν_1, ν_2, ν_3, ν_4, ν_5, ν_6, ν_7, ν_8 and ν_9. The vibrational frequencies corresponding to the emission bands λ 7346 and λ 7404 are taken as ν_{10} and ν_{11}. These eleven frequencies represent the remaining eleven normal modes of oscillation of the alumina lattice which include the six infra-red active frequencies also. As the values of the latter are not known accurately, no attempt has been made to assign some of the bands mentioned above as arising from the modulation by particular infra-red frequencies. ν_3, ν_6, ν_{10} and ν_{11} may be identified with the infra-red frequencies 244, 328-355, 847 and 909 cm.$^{-1}$ respectively. There is a group of 14 bands appearing on the Stokes side in the region λ 7428–7926 which are yet to be accounted for. There are no corresponding bands in the absorption spectrum. A possible explanation for the appearance of these bands is that they arise from the modulation of the electronic transitions of Cr^{+++} ions by some of the octaves and combinations of the vibration frequencies of the alumina lattice. Some of the more obvious assignments are indicated in column 8 of Table III.

In fluorescence and absorption, the lattice vibrations appear as diffuse bands and not as sharp lines. This is true even at low temperatures. The broadening can be explained on the basis that the loading of the lattice by the chromium ions gives rise to a perturbation of the vibrational modes. Part of the broadening may also be due to the fact that the principal electronic lines themselves have a finite width.

In conclusion, the author is grateful to Prof. Sir C. V. Raman for the loan of the specimens of alumina used in the present investigation and also for his kind interest in the work.

6. Summary

Using the λ 2536·5 mercury resonance radiation as exciter, the scattering of light in crystalline alumina has been investigated. The spectrum of the scattered light exhibits two Doppler-shifted components centred round the exciting line and seven Raman shifts. From the measured shift of the Doppler components the velocity of sound in alumina has been estimated. The appearance of seven Raman lines is shown to be in accord with the

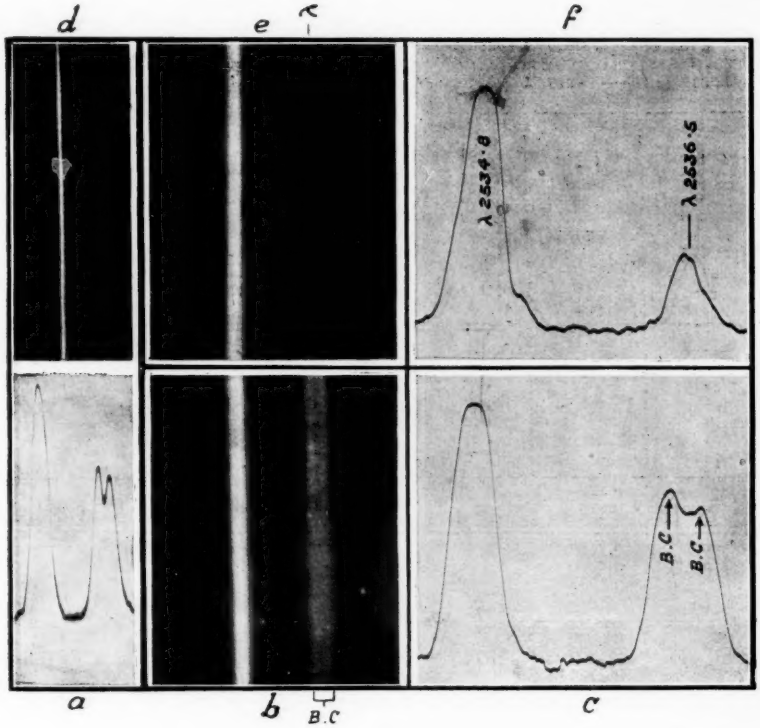

FIG. 1
B. C. = Brillouin components
λ = 2536·5 A. U.

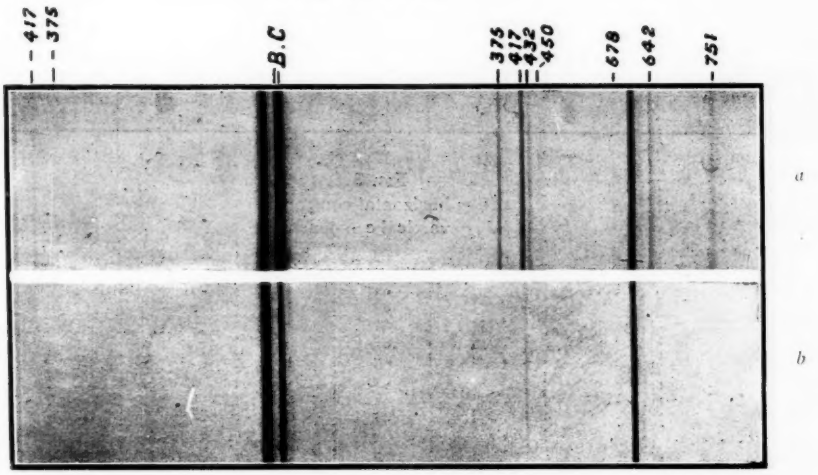

FIG. 2

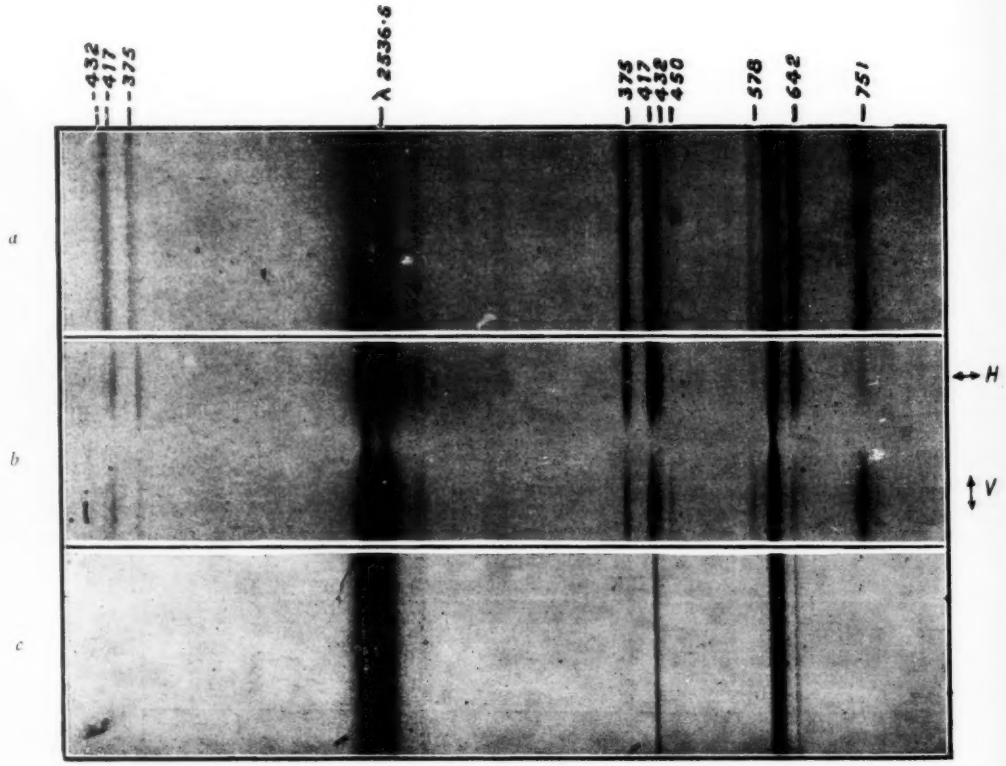

FIG. 3
H = horizontal component
V = vertical component

theoretical work of Bhagavantam and Venkatarayudu. The numerous bands appearing on both sides of the principal fluorescence doublet of ruby have been satisfactorily explained as arising from the combination of the vibration frequencies of the alumina lattice with the electronic transitions of the chromium ions.

References

1. Becquerel, J. .. *Phys. Zeits.*, 1907, **8**, 932;
   ——— .. *C. R.*, 1910, **151**, 859; 1911, **152**, 183.
2. Bhagavantam, S., and Venkatarayudu, T. .. *Proc. Ind. Acad. Sci.*, A, 1939, **9**, 224.
3. Boisbaudran .. *C. R.*, 1887, **106**, 452.
4. Coblentz .. *Investigations*, 1908, **5**, 17, 34.
5. Crookes, W. .. *Chem. News.*, 1887, **55**, 251; **56**, 59.
   ——— .. *Nature*, 1889, **39**, 542.
6. Deutschbein, O. .. *Ann. d. Phys.*, 1932, **14**, (*a*) 713, (*b*) 729.
   ——— .. *Phys. Zeits.*, 1932, **33**, 874.
   ——— .. *Zeit. f. Physik.*, 1932, **77**, 490.
   ——— .. *Ann. d. Physik.*, 1934, **20** 828.
7. du Bois and Elias .. *Ibid.*, 1908, **27**, 233.
8. du Fay .. *Hist. de l'acad. Roy. Paris*, 1724.
9. Hibben, J. H. .. *Proc. Nat. Acad. Sci.*, 1932, **18**, 535.
10. Krishnan, R. S. .. *Nature*, 1947, **160**, 26.
11. Mani, A. .. *Proc. Ind. Acad. Sci.*, A, 1942, **15**, 52.
12. Mendenhall and Wood .. *Phil. Mag.*, 1915, **30**, 316.
13. Meithe .. *Verk. d. Deutsch. Phys. Ges.*, 1907, **9**, 715.
14. Parodi, M. .. *C. R.*, 1937, **205**, 906.
15. Roop Kishore .. *Proc. Ind. Acad. Sci.*, A, 1942, **16**, 36.
16. Strong, J. .. *Phys., Rev.*, 1931, **38**, 1818.
17. Thosar, B. V. .. *Phil. Mag.*, 1938, **26**, 878.
    ——— .. *Phys. Rev.*, 1938, **54**, 233; 1941, **60**, 616.
    ——— .. *Journ. Chem. Phys.*, 1942, **10**, 246; 1944, **12**, 424.
18. Venkateswaran, C. S. .. *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 459.

Description of Plates

Plate XIX

Fig. 1. (*d*) and (*a*) the spectrum of the scattered light in alumina taken with the E 3 spectrograph and its microphotometer record.
(*b*) and (*c*) the same taken with the E 1 spectrograph and its microphotometer record.
(*e*) and (*f*) mercury spectrum taken with the E 1 spectrograph and its microphotometer record.

Fig. 2. (*a*) Raman spectrum of alumina taken with the E 1 spectrograph.
(*b*) Comparison spectrum of the mercury arc.

Plate XX

Fig. 3. (*a*) Raman spectrum of alumina taken with the E 3 spectrograph.
(*b*) The same taken with a double image prism and a nicol in the path of the scattered light.
(*c*) Comparison spectrum of the mercury arc.

THE RAMAN EFFECT IN TOPAZ AND ITS RELATION TO THE LUMINESCENCE SPECTRUM

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Received November 27, 1947

1. Introduction

The Raman spectrum of topaz was first photographed by K. S. Krishnan (1929) who reported only a single feeble Raman line with a frequency shift of 1053 cm.$^{-1}$ Nisi (1929) working with a clear crystal of topaz recorded two Raman lines. In a subsequent investigation, Nisi (1932) observed no less than 11 Raman lines including one with a large frequency shift, *viz.*, 3647 cm.$^{-1}$ He further showed that interchanging the direction of observation and illumination did not affect the relative intensities of the Raman lines which were generally influenced by both directions. Kopcewicz (1937) studied the influence of temperature on the Raman lines of topaz over the range from 20° C. to 500° C. Even by giving exposures of the order of 100 hours, Kopcewicz recorded only five Raman lines. He noticed that with increase of temperature the low frequency lines shifted towards the exciting line proportionately much more than the high frequency lines.

Judging from the complicated structure of topaz, $(AlF, OH)_2SiO_4$, it appeared that the results obtained by the above-mentioned authors are obviously incomplete. This is due to the feeble scattering power of topaz and also to the fact that the earlier workers used the λ 4046 and λ 4358 radiations of the mercury arc for exciting the Raman spectrum. It appeared likely that the use of the intense λ 2536·5 mercury resonance radiation as exciter would yield a more satisfactory Raman spectrum for the substance. This hope has been realised and the results obtained are presented in this paper together with a satisfactory explanation of the luminescence of topaz.

2. Results

While examining different specimens of topaz, it was found that only colourless samples are transparent to the λ 2536·5 radiation. A colourless specimen of topaz from a large collection of Ceylon gems presented to Sir C. V. Raman by Mrs. Jayawardane, was available for the present investigation. It was in the form of a prolate spheroid about 1″ long and $\frac{1}{2}$″ thick. The edges were flattened and polished. Both the Hilger medium and

large quartz spectrographs were employed for photographing the spectrum. In order to determine the frequency shifts of the lines an iron arc comparison spectrum was taken in all cases, partially overlapping the Raman spectrum.

TABLE I

Raman Spectrum of Topaz

Serial No.	Author (1947)		Nisi (1932)	Kopcewicz (1937)	Infra-red frequencies cm.$^{-1}$
	Frequency shift in cm.$^{-1}$	Intensity			
1	156	4			
2	167	2			
3	190	1		189	
4	241	8	241 (1)	232	
5	269	9	268 (4)	270	
6	287	7	285 (4)		
7	317	2			
8	335	4	336 (2)		
9	362	2			
10	374	2			
11	405	4	393 (2)		398
12	441	1			
13	459	4			*458*
14	490	2			*477*
15	520	5			510
16	550	2			550
17	558	4	560 (0)		
18	650	2			*652*
19	705	1			
20	770	1			
21	850	4	857 (4)		
22	874	1			
23	898	3			*897*
24	920	8	925 (4)	920	
25	934	10			932
26	940	2			*958*
27	985	6	983 (1)		1010
28	1162	4	1165 (0)		
29	1235–1280	0			
30	1355–1435	0			
31	3636	2			
32	3649	7	3647 (1)		3600

Photographs of the Raman spectrum of topaz taken with the medium and large quartz spectrographs are reproduced in Figs. 1 (*b*) and 2 (*b*) respectively. Using a fairly fine slit (0·05 mm.), exposures of the order of 36 hours were given when working with the medium spectrograph, while exposures of the order of 6 days were necessary for the bigger instrument. Figs. 1 (*a*) and 2 (*a*) represent the photographs of the mercury arc spectrum. The Raman spectrum of topaz exhibits 30 lines and 2 bands the frequency shifts of which together with the relative intensities are tabulated in Table I.

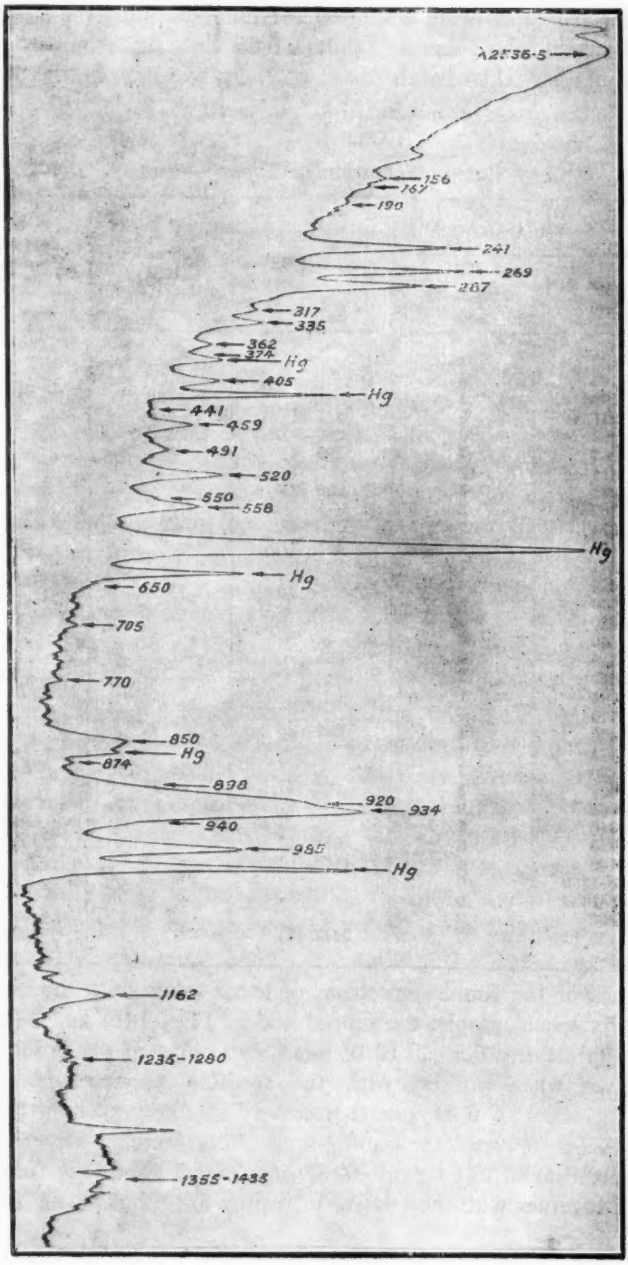

FIG. 3. The microphotometer record of the Raman Spectrum of topaz taken with the Hilger large quartz (E1) spectrograph

Note.—The fogging very near the exciting line is due to inefficient filtering.

The frequency shifts of the Raman lines reported by Nisi (1932) and by Kopcewicz (1937) are also included. About twenty Raman shifts have been recorded for the first time. The positions of the lines are marked in the figures. Some lines form closely spaced doublets. They are not easily discernible as distinct lines in the reproduced photographs. They are, however, more clearly identified in the microphotometer record reproduced in Fig. 3 above. The line with the frequency shift 934 cm.$^{-1}$ is the most intense one in the whole spectrum. The 3649 cm.$^{-1}$ line which was first reported by Nisi is extremely sharp and is followed by a weak companion on the shorter wave-length side. The low frequency lines are in general sharper than the lines in the high frequency shift region. This generalisation is not applicable to the lines 3636 and 3649 cm.$^{-1}$ The existence of a feeble line at about 1056 cm.$^{-1}$ reported by K. S. Krishnan and Kopcewicz has not been confirmed in the present investigation and consequently it is omitted from Table I.

3. Infra-Red Spectrum

The infra-red spectrum of topaz was first investigated by Coblentz (1908) who reported the appearance of three reflection maxima at 9·9 μ, 10·45 μ and 11·0 μ respectively. Schæfer, Matossi and Wirtz (1934) studied the infra-red reflection spectra of several silicates including that of topaz. They reported the existence of thirteen reflection maxima the corresponding wave-lengths being 9·9, 10·44, 10·75, 11·15, (15·00), 15·35, (15·60), 17·10, 18·20, 18·96, 21·0, 21·8 and 25·2 μ. Those given in brackets are doubtful. The frequencies in wavenumbers of the ten reflection maxima are entered in column 6 of Table I. Those shown in italics correspond to the more prominent reflection maxima. It is interesting to note that those frequencies which appear strongly in infra-red absorption are recorded only with feeble intensity in the Raman spectrum. The agreement between the observed Raman and infra-red frequencies can be taken to be satisfactory in view of the fact that the infra-red frequencies have been evaluated from positions of reflection maxima. Matossi and Brouder (1938) investigated the infra-red absorption spectra of several silicates including topaz in the short wave-length region. They have recorded 23 absorption maxima in topaz in the region from 7·4 μ to 1·45 μ. All the infra-red frequencies appearing in this region except those corresponding to the sharp maxima at 2·9 μ (3405 cm.$^{-1}$), 2·7 μ (3600 cm.$^{-1}$) and 2·6 μ (3850 cm.$^{-1}$) have been assigned as combinations and octaves of the fundamental infra-red frequencies obtained by Schæfer, Matossi and Wirtz (1934) and entered in column 6 of Table I. The strong absorptions at 2·94 μ, 2·78 μ and 2·6 μ

have been explained by them as arising from OH bands appearing with great intensity. The frequency shift of the middle OH band, namely $2 \cdot 78 \mu$ (3600 cm.$^{-1}$) coincides roughly with that of the Raman line at 3649 cm.$^{-1}$ Consequently the value is also entered in column 6 of Table I.

4. Discussion of Results

The crystal structure of topaz has been analysed using the X-ray method by Leonhardt (1924), Pauling (1928) and Alston and West (1928). Topaz is regarded as dialuminyl difluoro-silicate $(AlF)_2SiO_4$. The structure belongs to the orthorhombic class. X-ray investigations reveal that there are 4 molecules of $(AlF)_2SiO_4$ in each elementary parallelopiped. The structure is based upon a closest packing of oxygen atoms, though it is not one of the simple forms but a combination of the cubic and hexagonal closest packing. It is composed of linked octahedral groups around silicon as in other alumino-silicates. According to Bragg (1937), each alumina atom is surrounded by six atoms of which four belong to the SiO_4 group and the rest are fluorine atoms. It is suggested that in some specimens the F may be partly replaced by OH to form $(AlF,OH)_2 SiO_4$.

It is clear from the above analysis that topaz possesses very low symmetry and that each unit cell contains a large number of atoms. Consequently, nearly all the numerous possible modes of atomic vibration should be active in the Raman effect and also in infra-red absorption. The experimental results fully support the above conclusion. The line at 3649 cm.$^{-1}$ is a genuine Raman shift as it is observed both with λ 4046 and λ 2536·5 excitations. This line should be attributed to the OH oscillation and its appearance in the Raman spectrum of topaz clearly suggests that the molecular structure is $(AlF, OH)_2SiO_4$ and not $(AlF)_2SiO_4$. The recorded spectrum of topaz should exhibit the frequencies corresponding to all the nine characteristic modes of oscillation of the SiO_4 group which may not behave as a tetrahedrally symmetric group inside the crystal. A more complete and satisfactory interpretation of the Raman spectrum of topaz is not possible at present for want of full data on the Raman spectra of other complex silicates.

5. Raman Effect and its Relation to Luminescence

The foregoing results on the Raman spectrum of topaz are of interest in relation to the luminescence exhibited by certain varieties of topaz. Deutschbein (1932 *a*) examined the emission spectrum of topaz containing chromium phosphors both at room temperature and at liquid-air temperature (— 195° C.). The spectrograms taken by him have been schema-

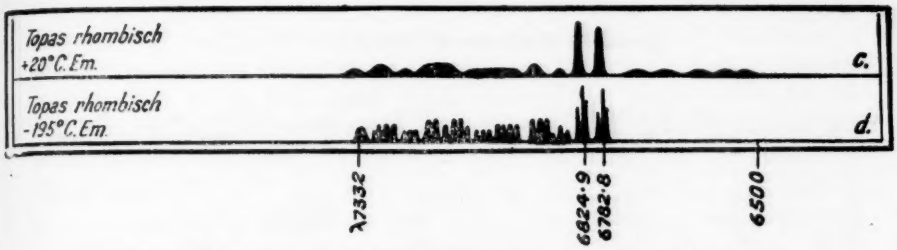

FIG. 4. Chart showing the luminescence spectrum of ptoaz reproduced from Deutschbein's paper

tically represented in the accompanying chart (Fig. 4). At 20° C., the luminescence spectrum consists of two broad and intense lines λ 6791·7 and λ 6832·7, accompanied by five broad bands on the shorter wave-length side and seven bands of varying width and intensity on the longer wave-length side of the principal doublet. At — 195° C. the principal doublet sharpens and each of its components is accompanied by two secondary lines which are absent in the spectrum taken at 20° C. At these low temperatures the bands on the shorter wave-length side of the principal doublet disappear completely from the fluorescence spectrum, while those on the longer wave-length side become sharp and exhibit some structure. Deutschbein identified 23 lines, each one of them being fairly broad. Their wave-lengths and frequencies as reported by Deutschbein are entered in Table II below. In a subsequent paper, Deutschbein (1932 *b*) explained the appearance of the principal doublet as due to the electronic transitions of the chromium ions present as impurity in the crystal. The 4 faint secondary lines accompanying the principal doublet on either side which are omitted from Table II have been ascribed by Deutschbein to an intra-molecular Stark effect. The principal electronic lines of Cr^{+++} are shifted towards shorter wave-length side by about 100 A.U. compared to those in ruby. Since the Stokes law was obeyed by the diffuse bands, Deutschbein suggested that they might arise from the superposition of the vibration frequencies of the ground material on the electronic transitions of the Cr^{+++} ions. On this basis, he showed that the frequency shifts of the bands λ 7271 and λ 6917 from the principal line R_1 were of the same order of magnitude as the two Raman shifts 911 and 260 cm.$^{-1}$ observed by Nisi (1929), which were the only ones known to exist at that time.

As more complete data on the Raman spectrum of topaz are made available by the present investigation, it is possible to give satisfactory assignments for all the vibrational bands observed by Deutschbein. These are

TABLE II

Emission Spectrum of Topaz at — 195° C.

Serial No.	Wavelength in A.U.	Wavenumber in cm.$^{-1}$	Intensity	Width in cm.$^{-1}$	Shift in cm.$^{-1}$ from R_1	Shift in cm.$^{-1}$ from R_2	Raman frequency
	6782·8	14739	9	10	Principal Line R_2		
	6824·9	14648	10	10	Principal Line R_1		
1	6860	14573	2	20		166	167
2	6873	14545	3	20		194	190
3	6893	14504	1	20		246	241
4	6903	14483	4	20	165		167
5	6917	14454	4	20	194		190
6	6936	14414	4	20	234		241
7	6970	14344	3	15		395	405
8	6985	14313	3	15	335		335
9	7000	14282	3	15	362		362
10	7012	14257	3	15	391		405
11	7032	14217	2	15	431		441
12	7045	14191	2	15	457		459
13	7059	14163	2	15	485		490
14	7080	14120	3	25	528		520
15	7102	14076	4	40	572		558
16	7131	14020	3	25		719	705
17	7162	13958	4	45	690		705
18	7215	13857	2	40	791		770
19	7255	13779	3	22	869		874
20	7271	13750	3	22	898		898
21	7288	13718	4	22	930		934
22	7299	13696	2	22	952		940
23	7332	13635	3	40	1013		985

4 Secondary electronic lines appearing in the neighbourhood of the principal doublet have been left out from the table.

indicated in Table II. As in the case of ruby, in topaz also, the most intense line of the principal doublet, *e.g.*, λ 6824·9, is mainly operative in producing the vibrational bands. Taking into consideration the finite width of the bands, the agreement between their frequency shifts from the principal doublet and the observed Raman shifts of topaz can be considered as very good. The loading of the lattice by the chromium ions must give rise to a perturbation of the vibrational modes and this would explain the fact that in luminescence, lattice vibrations appear as diffuse bands and not as sharp lines. The broadening might also be due to the fact that the principal electronic transitions themselves are broad to the extent of about 10 cm.$^{-1}$ and that the bands arising from the modulation of the principal line R_1 by certain lattice frequencies fall adjacent to those arising from the modulation of the principal line R_2 by other lattice frequencies.

It may be remarked that in luminescence and in the Raman effect, the vibrations of the crystal lattice are excited by entirely different mechanisms, and yet, as we have seen, there is complete correspondence between the frequency shifts of the vibrational bands appearing in luminescence and the Raman shifts of topaz. This result is very significant and has far-reaching consequences. According to the Born lattice dynamics, the appearance of sharp lines in the first order Raman spectrum of any crystal is explained as due to some kind of a selection rule which picks out only certain frequencies from the continuous vibration spectrum of the lattice. There is no reason to suppose that the same type of selection rule should be operative in luminescence also. In fact, the entire vibration spectrum should appear as a continuous band in emission without showing any fine structure of the kind actually observed. It follows therefore that what is actually recorded in luminescence and in Raman effect indicates the real nature of the vibration spectrum, namely that it consists of a set of discrete frequencies.

The author is grateful to Professor Sir C. V. Raman for the loan of the crystal of topaz and also for his kind interest in the work.

6. Summary

The Raman effect in topaz has been investigated using the 2536·5 mercury resonance radiation as exciter. The spectrum exhibits 32 Raman shifts of which no less than 21 have been recorded for the first time. The results obtained are discussed with special reference to the infra-red absorption and luminescence spectra of topaz. The significance of the complete correspondence noticed between the Raman shifts and the frequency shifts of the vibrational bands in luminescence is pointed out.

References

1. Alston, N. A., and West, J. .. *Zeits. f. Kristal.*, 1928, **69**, 149.
2. Bragg, W. L. .. *Atomic Structure of Minerals*, 1937, 172.
3. Deutschbein, O. .. *Ann. d. Physik*, 1932 (*a*), **14**, 729.
———— .. *Zeits. f. Physik*, 1932 (*b*), **77**, 490.
4. Kopcewicz .. *Journ. de Physique et Rad.*, 1937, **8**, 6.
5. Krishnan, K. S. .. *Ind. Jonrn. Phys.*, 1929, **4**, 131.
6. Leonhardt .. *Zeits. f. Kristal.*, 1924, **59**, 216.
7. Matossi, F., and Brouder, O. .. *Zeits. f. Phys.*, 1938, **111**, 1.
8. Nisi, H. .. *Proc. Imp. Acad. Tokyo*, 1929, **5**, 127.
———— .. *Proc. Phys. Math. Soc. Japan*, 1932, **14**, 214.

9. Pauling, L. .. *Proc. Nat. Acad. Sci.*, 1928, **14**, 603.

10. Schæfer, Cl., Matossi, F., and Wirtz, K. .. *Zeit. f. Phys.*, 1934, **89**, 210.

Description of Plate

Plate XXI

Fig. 1. (*a*) Mercury spectrum taken with the medium quartz E 3 spectrograph.

(*b*) Raman spectrum of topaz taken with the same instrument.

Fig. 2. (*a*) Mercury spectrum taken with the large quartz E 1 spectrograph.

(*b*) Raman spectrum of topaz taken with the same instrument. Fogging very near the exciting line is due to inefficient filtering.

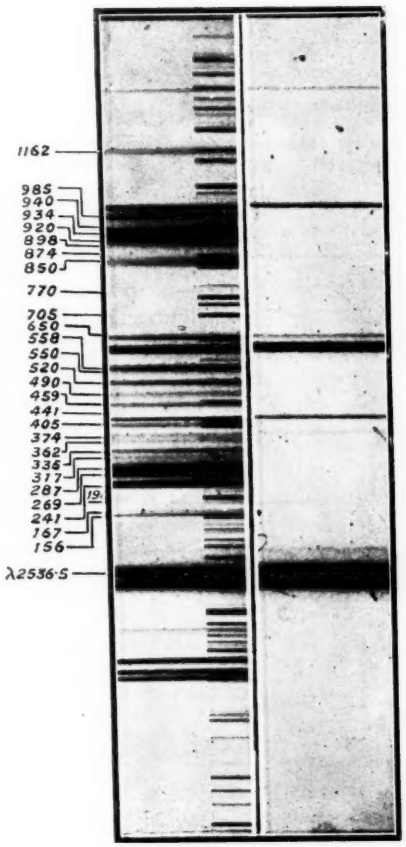
1162
985
940
934
920
898
874
850
770
705
650
558
550
520
490
459
441
405
374
362
336
317
287
269
241
167
156
λ2536·5
b
a

FIG. 1

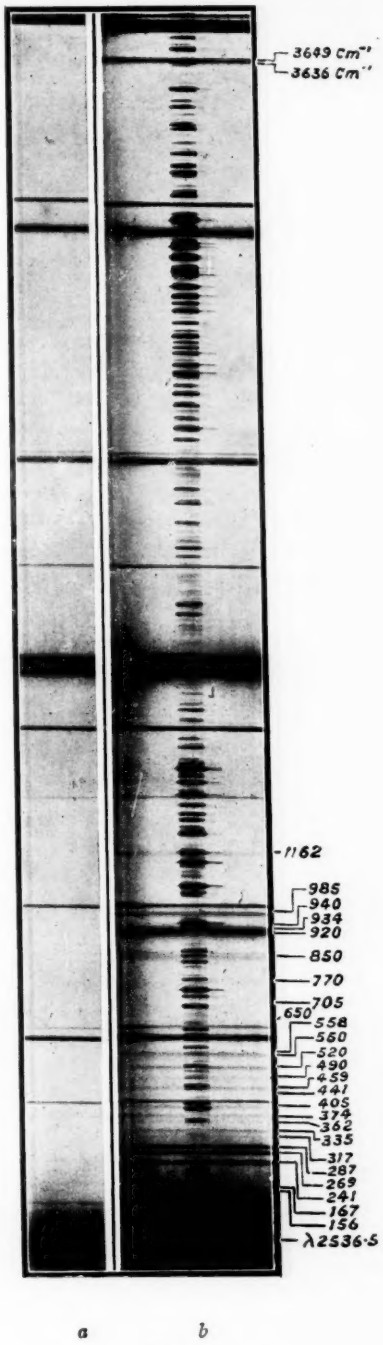
3649 Cm⁻¹
3636 Cm⁻¹
1162
985
940
934
920
850
770
705
650
558
550
520
490
459
441
405
374
362
335
317
287
269
241
167
156
λ2536·5
a
b

FIG. 2

THE INFRA-RED ABSORPTION SPECTRUM OF DIAMOND AND ITS VARIATIONS

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

In a previous work (Ramanathan, 1946) the infra-red absorption spectra of four typical diamonds were investigated in the region between 750 and 2200 wavenumbers. Due to the inadequate resolution of the spectrometer used, the curves reproduced there do not show much detail in the region between 1500 and 2200 cm.$^{-1}$ The present work was therefore undertaken with a view to improve upon the technique and to examine as many cleavage plates of diamond as possible in the region of the spectrum 750–4000 cm.$^{-1}$ It was also the aim of the present research to investigate the local variations in infra-red absorption spectrum within its area of a typical specimen exhibiting patterns of luminescence and ultra-violet transparency.

2. Improvements in Technique

Since the author's previous studies mentioned above, several improvements in technique have been made with a view to increase the resolving power of the instrument. To prevent undue heating of the surroundings, the original globar source was dispensed with and an ordinary incandescent filament source, enclosed in an aluminium box with an aperture for the exit of radiation, substituted. The dispersing device now being used is a 60° prism of rocksalt with refracting faces 2″ by 1½″ in place of the 54° prism with 2″ square faces previously used. Nearly a tenfold increase in the sensitivity of the Boy's radiomicrometer has been achieved by the use of Hutchin's alloys for the thermocouple and a fine quartz fibre for the suspension. The instrument mounted on rubber shock absorbers on a heavy concrete platform inside an airtight chamber is very steady in quiet weather during which readings can be taken correct to a millimetre or two. The infra-red spectrometer was calibrated by employing the method described by Rawlins and Taylor (1929). The 5461 Å radiation of the mercury arc and the CO_2 emission maximum at $4{\cdot}38\,\mu$ from a Bunsen flame have been used as calibration wave-lengths. The procedure adopted for obtaining the absorption curves has already been described in the previous work.

3. Results

With the above arrangement, the infra-red absorption spectra of nine cleavage plates of diamond have been investigated and the results obtained are described below.

(*a*) *The* 1500–2700 *Band.*—This region comes first for consideration because all diamonds irrespective of their other physical properties exhibit a band in this region with a number of absorption maxima. In comparing the relative strengths of any absorption band in different diamonds, one has of course got to consider the thicknesses of the specimens. It is also necessary to take into account the small variations in transmission which may result from the slight curvature of its surfaces. Allowing for the discrepancies resulting from these two facts, it is seen that the absorption band in this region shows no observable variations in strength or structure from diamond to diamond (see Figs. 1 to 9).

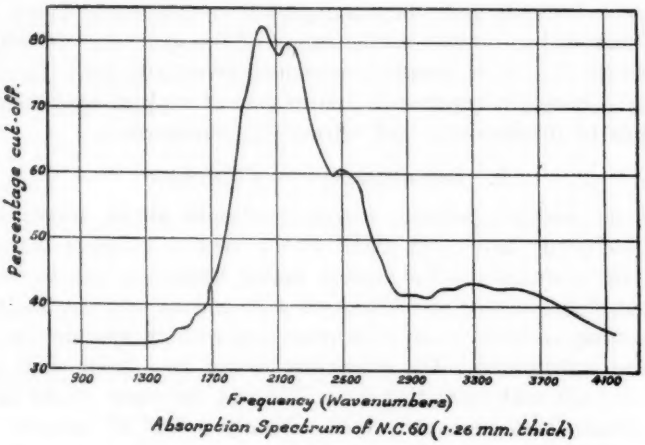
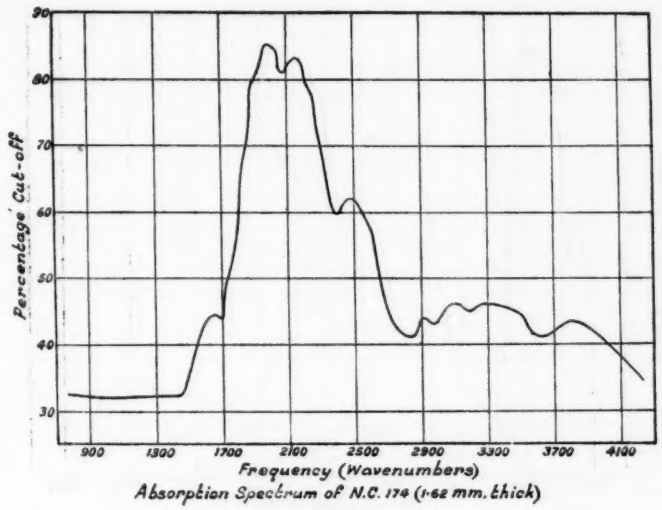


Fig. 1

All the diamonds without exception exhibit in this band two very strong absorption maxima centred at 2010 and 2170 wavenumbers and a third one at 2470 cm.$^{-1}$ which is much weaker than the former two. In addition a number of step-like falls in absorption have been observed in many diamonds in this region. This feature appears in the curves reproduced for most of the diamonds and the effect therefore appears to be a genuine one. The step-like falls or inflexions are not so prominent in the curves of the thicker diamonds, while in the thinnest of them investigated, they are in a few cases even resolved into peaks of absorption. The approximate frequencies

corresponding to these points of inflexion are 2300 cm.$^{-1}$, 1900 cm.$^{-1}$, 1800 cm.$^{-1}$, 1660 cm.$^{-1}$ and 1560 cm.$^{-1}$



Absorption Spectrum of N.C. 174 (1·62 mm. thick)

FIG. 2

Absorption Spectrum of N.C. 177 (0·85 mm. thick)

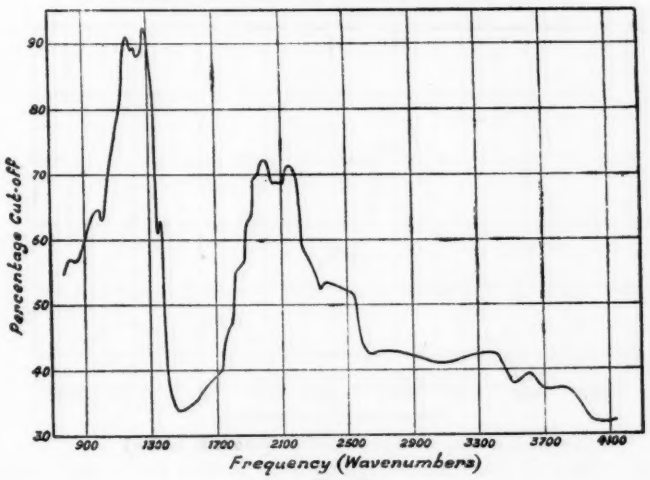
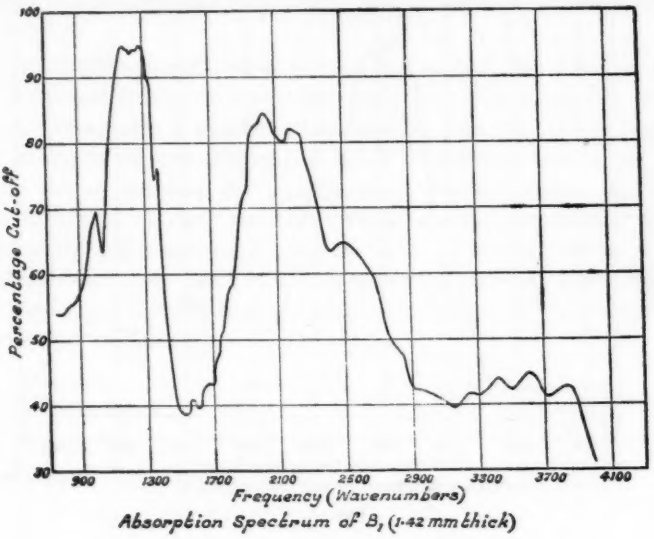


FIG. 3

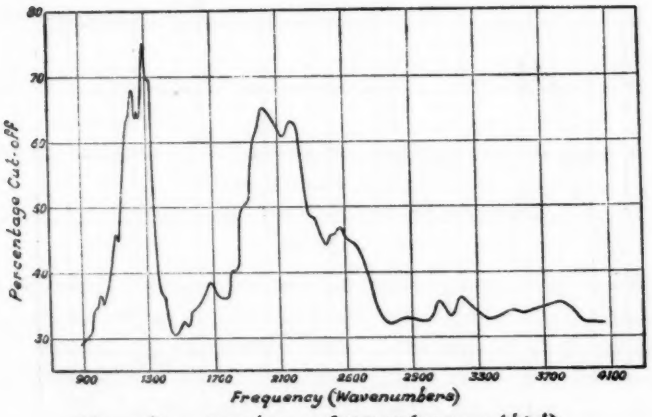
(*b*) *The* 750–1400 *cm.*$^{-1}$ *Band.*—The variations in the intensity of this band are shown most strikingly by the series of curves reproduced for eight of the diamonds investigated (Figs. 1 to 8). The band is completely absent

in the diamonds N.C. 60 and N.C. 174 (Figs. 1 and 2 respectively) which after allowing for reflection of radiation from the two surfaces of a cleavage



Absorption Spectrum of B_1 (1·42 mm thick)

FIG. 4



Absorption Spectrum of N.C 74 (0·66mm. thick)

FIG. 5

plate, are found to be completely transparent in the region between 750 and 1400 cm.$^{-1}$ It is strongest in the weakly blue-fluorescent diamonds N.C. 175

B_1, N.C. 74 and N.C. 73 (Figs. 3, 4, 5 and 6 respectively), somewhat weaker in the strongly blue-fluorescent diamond N.C. 79 and weakest in the diamond N.C. 110 exhibiting a yellow luminescence. The extent of variation in the

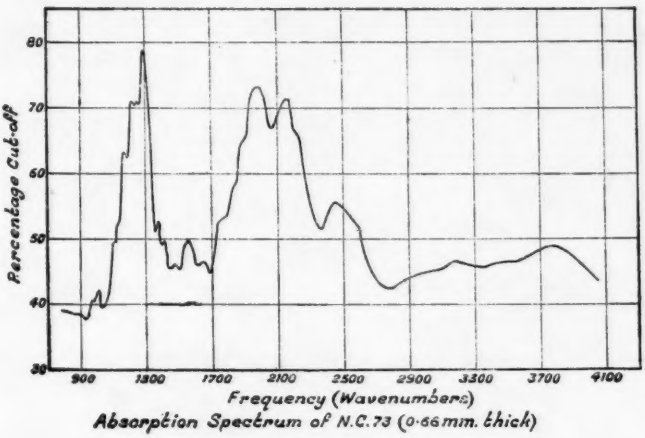


FIG. 6

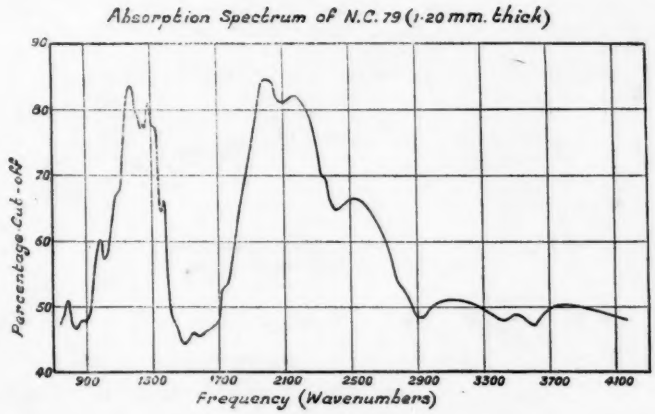


FIG. 7

strength of the band can be appreciated from Table I which shows the coefficient of absorption at three of the peaks in this band (1000 cm.$^{-1}$, 1170 cm.$^{-1}$ and 1290 cm.$^{-1}$) together with those at the three peaks 2010 cm.$^{-1}$, 2170 cm.$^{-1}$ and 2470 cm.$^{-1}$ shown for comparison.

TABLE I

Intensities of Absorption Peaks in Various Diamonds

Catalogue Number of Diamond	Coefficient of Absorption at the various peaks (per cm.)					
	1000 cm.$^{-1}$	1170 cm.$^{-1}$	1290 cm.$^{-1}$	2010 cm.$^{-1}$	2170 cm.$^{-1}$	2470 cm.$^{-1}$
N. C. 177 ..	8·1	24·0	30·0	10·9	10·4	4·8
B_1 ..	5·8	17·6	18·0	10·4	9·5	4·8
N. C. 74 ..	1·6	10·2	15·7	10·6	9·7	4·2
N. C. 73 ..	3·0	9·8	18·0	14·5	13·5	7·0
N. C. 79 ..	4·7	12·0	10·9	12·6	11·4	6·2
N. C. 110 ..	2·1	6·6	5·3	12·8	11·9	5·1
N. C. 175 (*a*)	..	..	1·6	12·2	10·9	5·1
N. C. 175 (*b*)	..	..	0·7	11·8	10·4	4·9
N. C. 60 ..	0·4	0·4	0·4	10·8	9·8	4·6
N. C. 174 ..	0·2	0·2	0·2	9·6	8·8	3·8

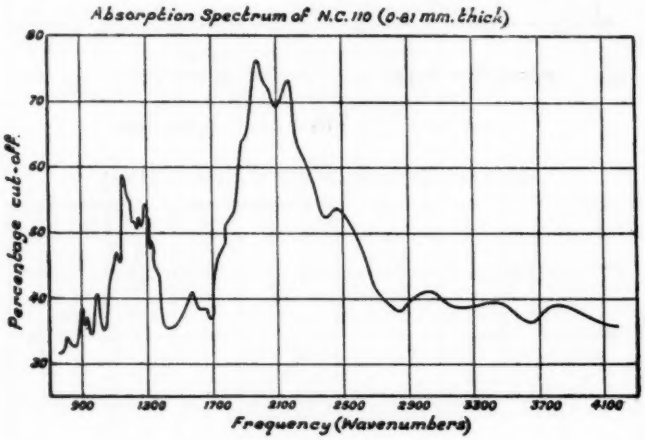


FIG. 8

In comparing the intensities of any absorption band in various diamonds, one must take into account the optical imperfections of the specimens which increase the apparent coefficient of absorption in some cases. That such an increase is caused by the irregularities is obvious from the fact that in some diamonds the coefficient of absorption comes out higher for all the three peaks in the 5μ band (1500-2700 cm.$^{-1}$) and if proportionately

decreased, they become equal to the values obtained for the other diamonds which are free from such imperfections.

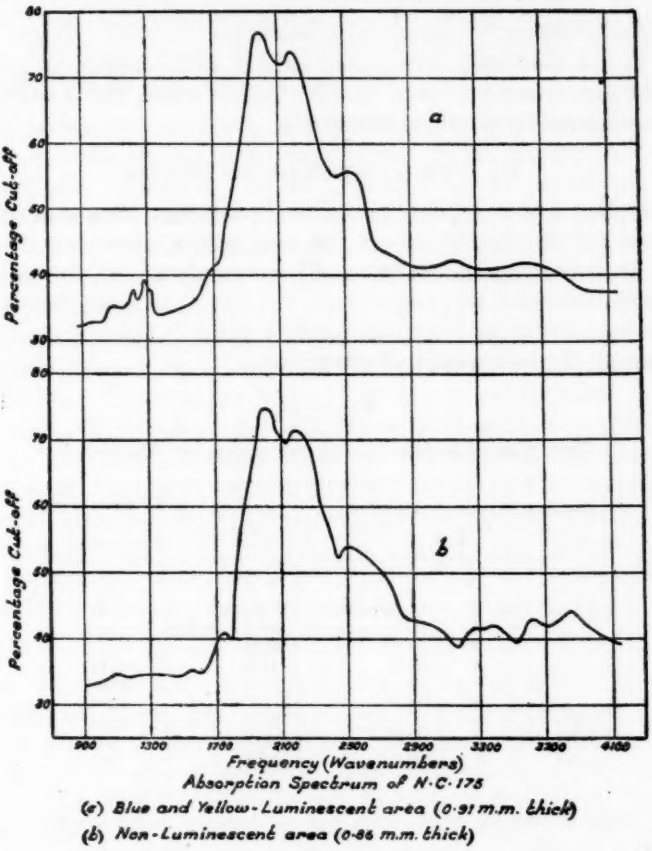


FIG. 9

The various absorption maxima observed in the previous work, are recorded here under better resolution. The inflexion at 1330 wavenumbers has also been observed in most of the diamonds exhibiting this band.

The diamond N.C. 175 shows a pattern of luminescence and so has been used for investigating the spectral character of the local variations. (*a*) and (*b*) denote respectively the luminescent and non-luminescent areas in the diamond. The remarkable changes observed in the absorption spectrum can be seen from Figs. 9 (*a*) and (*b*). The non-luminescent area shows no

absorption band in the region 750–1400 cm.$^{-1}$ A very weak band is howeve exhibited by the luminescent area, the structure of the band being essentially the same as in most other diamonds.

(*c*) 2700–4000 *cm.*$^{-1}$ *region.*—The absorption in this region is very weak. All the diamonds investigated exhibit some absorption bands, but due to the inadequate resolution of the rocksalt prism, the positions of the maxima could not be measured accurately.

4. Interpretation of the Results

In another paper appearing in these *Proceedings* (Ramanathan, 1947), expressions for the frequencies of the nine modes of atomic vibration in diamond have been derived in terms of 8 independent force constants. The frequencies used there in evaluating the constants, obtained from the most reliable spectroscopic data are contained in Table II below together with a description of the nine modes of vibration.

Table II

The Nine Fundamental Frequencies of Diamond

Frequency Sequence	Degeneracy	Oscillating Units	Direction of oscillation	Observed and calculated Frequencies
				cm.$^{-1}$
I ..	3	The two lattices	Arbitrary	1332
II ..	8	(111) planes	[01$\bar{1}$] direction	1250
III ..	6	(100) ,,	[011] ,,	1232
IV ..	4	(111) ,,	[111] ,,	1149
V ..	3	(100) ,,	[100] ,,	1088
VI ..	3	(100) ,,	[100] ,,	1088
VII ..	4	(111) ,,	[111] ,,	1008
VIII ..	6	(100) ,,	[01$\bar{1}$] ,,	752
IX ..	8	(111) ,,	[01$\bar{1}$] ,,	620

From the table it can be seen that the absorption band appearing in the region 750–1400 cm.$^{-1}$ is due to the fundamental frequencies, the one at 1500–2700 cm.$^{-1}$ as due to second-order effects and the band at 2700–4000 cm.$^{-1}$ as due to third-order effects. We shall not deal with the third order band in this paper as the data available regarding it are very meagre.

The two strongest absorption maxima appearing at 2010 and 2170 cm.$^{-1}$ in the second-order band are obviously due to the octaves of the modes VII and V and VI with frequencies of 1008 and 1088 cm.$^{-1}$ respectively. The broad maximum around 2470 cm.$^{-1}$ whose doublet character is revealed in many of the curves, is evidently due to the octaves of modes II and III with frequencies of 1232 and 1250 cm.$^{-1}$ respectively, as also their summation.

In addition, an inflexion appearing at about 2300 cm.$^{-1}$ has to be interpreted as the octave of mode IV (1149 cm.$^{-1}$) which is not well resolved owing to its falling on the steep portion of a much stronger band at 2170 cm.$^{-1}$ The inflexions appearing on the lower frequency side of 2010 cm.$^{-1}$ can be interpreted as the combinations of the two low frequency modes with those having higher frequencies.

If the various modes of vibration are dynamically independent of each other, then as pointed out in the paper referred to, mode I of Table II representing the fundamental lattice frequency should be inactive in the non-luminescent diamonds and active in others. The other modes II to IX should be inactive in all diamonds as fundamentals, due to the reversal of phase of the vibrations in the successive layers of atoms. Owing to anharmonicity, however, there will be some coupling between the various modes as a result of which, the activity of the fundamental lattice frequency will be necessarily followed by the activity of all the other modes situated in the neighbourhood. The coupling between the various modes might also result in slight shifts of the absorption maxima as well as in the appearance of absorption in regions midway between two fundamental frequencies. The strong peak at 1290 cm.$^{-1}$ situated midway between 1330 and 1250 cm.$^{-1}$ has probably such an origin. The rapid fall of intensity of the various peaks with increasing distance from mode I adds support to the above explanation of their appearance. The peak at 1375 cm.$^{-1}$ is the combination of modes VIII and IX of Table II, rendered active owing to its contiguity with the mode I.

From the curves reproduced for the six diamonds exhibiting the first-order band, it will be seen that it is most striking in diamond N.C. 177 which has got the feeblest blue luminescence and is characterised by the maximum homogeneity of structure. The diamonds in which the band is absent (N.C. 60 and N.C. 174, Figs. 1 and 2) are, on the contrary, characterised by inhomogeneities in structure and optical birefringence. The presence of the band in some diamonds and its absence in others is therefore to be attributed neither to the presence of impurities, nor to crystal imperfections, but to a deeper reason, *viz.*, a fundamental difference in crystal symmetry, which is tetrahedral in one case and octahedral in the other.

It is observed, however, that mosaicity of structure can influence an absorption band by giving rise to changes in its intensity distribution. In the absorption spectra of the strongly luminescent diamonds N.C. 79 and N.C. 110, the intensity distribution in the entire band is different from that for the other diamonds. The strongest peak in these two curves is the one

at 1170 cm.$^{-1}$ It will be seen from Table II that this frequency corresponds to the normal oscillation of the octahedral planes of atoms with the closely spaced layers moving with the same phase. If interpenetration of structures having different crystal symmetry takes place in such manner that they appear as alternate finely spaced laminæ parallel to the octahedral planes of the diamond, then the electric moment developed in neighbouring layers would no longer cancel out for mode IV (1149 cm.$^{-1}$) and mode VII (1008 cm.$^{-1}$). It has been shown by Ramachandran (1946) that in most luminescent diamonds, interpenetration of the different structures takes place with the laminations parallel to the octahedral planes of the diamond.

Acknowledgement

My grateful thanks are due to Prof. Sir C. V. Raman for his kind guidance and encouragement and also for the loan of the diamonds used in this investigation.

Summary

The infra-red absorption spectra of nine cleavage plates of diamond have been investigated in the region of frequencies between 750 and 4000 cm.$^{-1}$ and their observed spectral behaviours have been elucidated. While the second-order spectrum is similar for all diamonds, the first-order spectrum shows large variations. From the nature of these variations it is concluded that the first-order activity is due neither to chemical impurities nor to mosaicity of structure, but must be attributed to the tetrahedral symmetry of structure possessed by such diamonds.

References

1. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, A, 1946, **24**, 65.
2. Ramanathan, K. G. .. *Ibid.*, 1946, **24**, 150.
3. ———— .. *Ibid.*, 1947, **26**, 493.
4. Rawlins and Taylor .. *Infra-Red Analysis of Molecular Structure*, 1929.

THE EMISSION AND ABSORPTION SPECTRA OF LUMINESCENT DIAMONDS

By K. G. Ramanathan

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received November 29, 1947

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Investigations made at this Institute by Dr. P. G. N. Nayar (1942) and Miss Anna Mani (1944) have shown that valuable information regarding the vibration spectrum of diamond is furnished by the study of the emission and absorption spectra of specimens which exhibit a blue luminescence under irradiation. For this purpose, it is necessary to cool the diamond to liquid-air temperature and record the emission or the absorption spectrum, as the case may be, under adequate resolving power. The vibration spectrum is then recorded in association with an electronic transition appearing at λ 4152, as a system of subsidiary bands at longer wavelengths in emission and at shorter wavelengths in absorption. Another system of vibration bands, not so well-defined, appears in association with an electronic line at λ 5032 in the case of diamonds which give a yellow or green luminescence. Numerous spectrograms showing these effects have appeared in papers published earlier in these *Proceedings*.

The principal line at λ 4152 is really a doublet, the separation of its components varying considerably with different specimens. Diamonds in which the components of the doublet are close together and sharp are naturally those most suitable for exhibiting clearly the discrete character of the vibration spectrum. Likewise, it is such diamonds which exhibit best the discrete structure of the vibration spectrum in absorption. It is necessary further to use a sufficient thickness for absorption. To obtain spectrograms capable of exhibiting the details clearly in a half-tone reproduction is largely a matter of photographic technique, and it cannot be said that the spectrograms published earlier in these *Proceedings* have been wholly satisfactory in this respect. The spectrograms and microphotometer records reproduced with this note are, it is hoped, somewhat better and they are intended to serve as demonstrations of the nature of the vibration spectrum of diamond.

Fig. 1 shows the emission spectrum of diamond reproduced as a negative together with a microphotometer record. The frequency shifts from the electronic emission at λ 4152 are also shown marked on the spectrogram

as well as on the microphotometer record. As shown in another paper appearing in these *Proceedings* (Ramanathan, 1947) there are eight distinct frequencies in the vibration spectrum. These are indicated against the microphotometer record. The two lowest, *viz.*, 752 cm.$^{-1}$ and 620 cm.$^{-1}$, are oscillations appearing in a region of frequency which is overlapped by the elastic vibration spectrum and is strongly perturbed thereby. They are therefore recorded as diffuse bands closely adjacent to each other. This is also evident in the absorption spectra reproduced as Figs. 2 and 3 in the plate. The absorption spectra have been photographed with an "intermediate" quartz spectrograph. An instrument of greater dispersion and resolution would probably have been more satisfactory. The microphotometric record in Fig. 2 (*b*) shows the two absorption lines at 1008 and 1088 cm.$^{-1}$ which appear much more clearly as emission lines in Fig. 1.

In conclusion the author is thankful to Sir C. V. Raman for his kind interest in the work.

Summary

Photographs of the emission and absorption spectra of blue-luminescent diamonds together with their microphotometric records are reproduced showing the discrete structure of the vibration spectrum.

References

1. Mani, Miss Anna .. *Proc. Ind. Acad. Sci.*, A, 1944, **19**, 231.
2. Nayar, P. G. N. .. *Ibid.*, 1942, **15**, 293.
3. Ramanathan, K. G. .. *Ibid.*, 1947, **26**, 481.

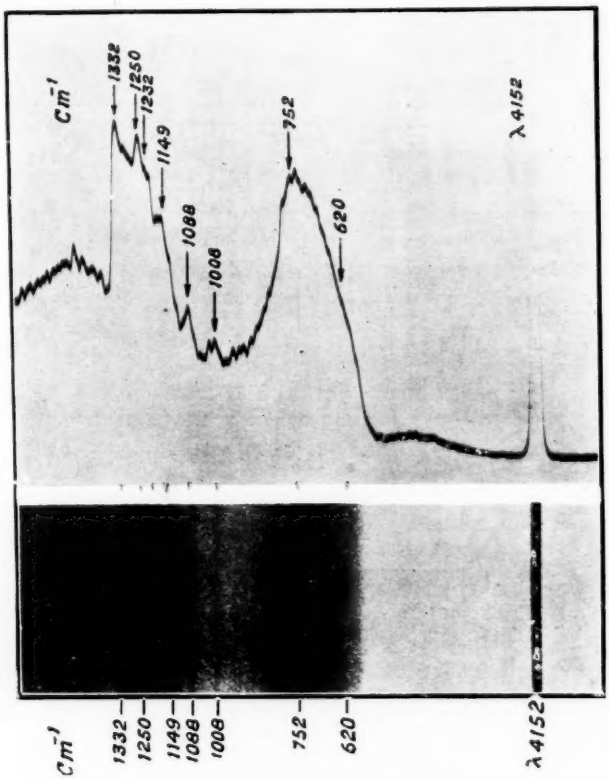


FIG. 1

The Emission Spectrum of Blue-Luminescent Diamond

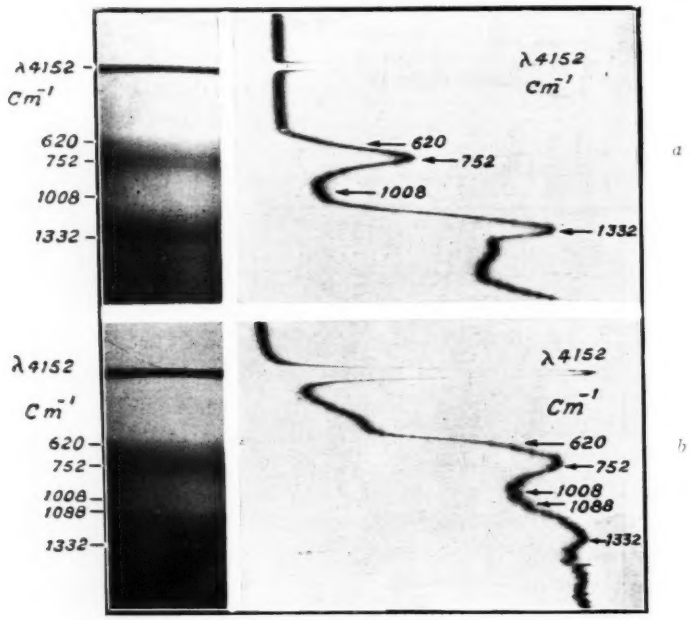


FIG. 2

The Absorption Spectrum of Blue-Luminescent Diamond

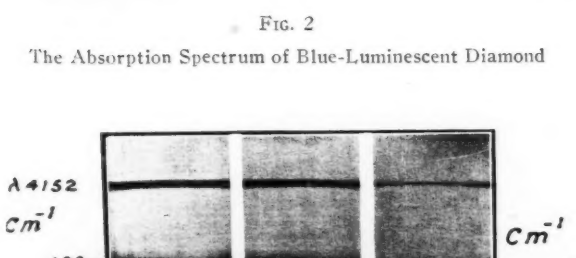


FIG. 3

The Absorption Spectrum of Blue-Luminescent Diamond

DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part I. Diamond

By K. G. Ramanathan

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Received October 31, 1947

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

The investigation of the possible modes and frequencies of vibration of the atoms in diamond about their positions of equilibrium is a necessary step for the interpretation of the Raman and infra-red spectra of this solid. Such an investigation is also essential for the interpretation of the emission and absorption spectra of luminescent diamonds at low temperatures and indeed also the other physical properties in which the vibrations of the atoms are involved. The spectroscopic behaviour of diamond has during recent years been thoroughly investigated at Bangalore by the several distinct methods mentioned above. In particular, the present author has recently carried out a detailed experimental study (1946, 1947) of the infra-red absorption spectra of numerous samples of diamond. It has accordingly become necessary to consider in some detail, the nature of the vibration spectrum of this substance.

According to the new theory of crystal dynamics recently put forward by Sir C. V. Raman (1943), the structure of diamond is capable of nine independent normal modes of vibration out of which the frequencies of two are the same, thus giving rise to a spectrum having eight numerically different vibration frequencies. Following Nagendra Nath (1934), Bhagavantam (1943) and Chelam (1943) have derived expressions for the frequencies of vibration of the various modes. But their treatment of the problem with three constants alone to represent the interatomic forces is inadequate. A more general and rigorous dynamical treatment of the problem is obviously called for, and this has been carried out in the present work on the lines indicated by Sir C. V. Raman in his theory of the dynamics of crystal lattices.

2. Description of the Modes

The new theory of crystal dynamics leads to the result that the structure of a crystal consisting of p non-equivalent atoms in each unit cell is capable

of $(24p-3)$ modes of vibration, out of which $(3p-3)$ represent vibrations in which the dynamic repeating pattern is the unit cell of the crystal. The remaining $21p$ modes represent vibrations in which the dynamic repeating unit is a super-cell having twice the linear dimensions of the unit cell. In the case of a face-centred cubic lattice having one atom per unit cell, it can be shown that the normal and tangential oscillations of the octahedral planes of atoms and the normal and the tangential oscillations of the cubic planes of atoms having degeneracies of 4, 8, 3 and 6 respectively, correspond to the 21 degrees of freedom representing the vibrations of the superlattice. In a case like diamond where there are two non-equivalent atoms in the unit cell, there are two possibilities corresponding to every one of the above four distinct modes of the face-centred cubic lattice, since the two non-equivalent atoms in the unit cell can now move either in the same phase or in opposite phases. In adddition, there will be one other frequency corresponding to the $(3p-3)$ modes, having a degeneracy of 3 which represents the oscillation of the two interpenetrating lattices of carbon atoms against each other, thus making up a total of nine independent modes having degeneracies of 4, 4, 8, 8, 3, 3, 6, 6 and 3. However, because of the numerical equivalence of the frequencies of the two triply degenerate modes of the superlattice, there will be only eight distinct frequencies in the vibration spectrum. The 45 degrees of freedom together with three transitions make up 48 which agrees with the number of degrees of freedom to be expected for the 16 atoms in a supercell having twice the linear dimensions of the unit cell. Table I

TABLE I

Sequence	Degeneracy	Oscillating units	Direction of motion	Relative phase of nearest layers	Operative Force-constant	Observed frequencies
						cm.$^{-1}$
I	3	The two lattices	Arbitrary	Opposite	$P-4Q+4S+8U-12\Sigma$	1332
II	8	Octahedral planes	[011]	Opposite	$P-2Q-2R+4W+6\Sigma+6\Omega$	1250
III	6	Cubic ,,	[011]	*Same	$P-4R-4S-12\Omega$	1232
IV	4	Octahedral ,,	[111]	Same	$P+2Q-4R-8W-6\Sigma+12\Omega$	1149
V	3	Cubic ,,	[100]	Opposite	$P+4S-8U$	1088
VI	3	Cubic ,,	[100]	Same	$P+4S-8U$	1088
VII	4	Octahedral ,,	[111]	Opposite	$P-2Q+4R-8W+6\Sigma-12\Omega$	1008
VIII	6	Cubic ,,	[011]	*Opposite	$P+4R-4S+12\Omega$	752
IX	8	Octahedral ,,	[011]	Same	$P+2Q+2R+4W-6\Sigma-6\Omega$	620

* See text for some explanatory remarks in these two cases.

contains a full description of the nine normal modes of vibration arranged in a descending sequence of the magnitudes of their frequencies determined as explained later.

3. The Equations of Motion

Since in any particular normal mode of vibration of any conservative dynamical system, all the particles vibrate with the same frequency, it is enough, in our present case, if we consider the equation of motion of any one atom, in order to obtain expressions for the frequencies of vibration of all the different modes. It is necessary here to decide as to how many of the neighbouring atoms are to be taken account of in deriving the equations of motion of a particular atom. There can be no question that the influence of the neighbouring atoms decreases rapidly as we go to the more and more distant ones. There is therefore no reason why we should not confine our attention to a limited number of neighbours in framing the equations of motion of a particular atom. In the present treatment, we shall take account of the influence of 28 atoms nearest to the one under consideration, these falling into three groups comprised of 4, 12 and 12 atoms respectively, situated at the same distance from the particular atom. We shall suppose this latter to be situated at the origin of a Cartesian co-ordinate system having its three axes along the three cube directions. Also let the suffix 0 represent this atom in what follows. Then the four atoms (1 to 4) situated at the ends of the tetrahedral axes are the nearest neighbours. The point 0 is common to twelve cube faces, four of them parallel to YZ, four to ZX and the remaining four to the XY planes of the co-ordinate system. The twelve atoms at the face centres of these twelve cube faces (5 to 16) represent the next-nearest neighbours of atom 0. The positions of the twelve atoms (17 to 28) can be arrived at by the translations of the four nearest neighbours, by the length of the edge of the unit cube along x, y and z axes in positive or negative directions according as atom 0 is situated in positive or negative directions of the co-ordinate system with respect to these atoms. The co-ordinates of all the 28 neighbours in fractions of the length of the edge of the unit cube, are contained in Table II.

Let x, y, z denote the displacements of the atom 0 and x_i, y_i, z_i, the displacements of the 28 neighbours from their equilibrium positions at any instant of time t. Then, if m denotes the mass of the carbon atom, the three equations of motion of atom 0 are:—

$$m\frac{d^2x}{dt^2} - x\,F_{xo}^{xo} = \sum_1^{28} x_i F_{xi}^{xo} + \sum_1^{28} y_i F_{yi}^{xo} + \sum_1^{28} z_i F_{zi}^{xo} \qquad (1)$$

$$m\frac{d^2y}{dt^2} - y\,F_{yo}^{yo} = \sum_1^{28} x_i F_{xi}^{yo} + \sum_1^{28} y_i F_{yi}^{yo} + \sum_1^{28} z_i F_{zi}^{yo} \qquad (2)$$

$$m\frac{d^2z}{dt^2} - z\,F_{zo}^{zo} = \sum_1^{28} x_i F_{xi}^{zo} + \sum_1^{28} y_i F_{yi}^{zo} + \sum_1^{28} z_i F_{zi}^{zo} \qquad (3)$$

TABLE II

Showing the Co-ordinates of the 29 atoms

Atom No.	x	y	z	Atom No.	x	y	z
0	0	0	0				
1	¼	¼	¼	2	¼	−¼	−¼
3	−¼	¼	−¼	4	−¼	−¼	¼
5	0	½	½	6	0	−½	−½
7	0	½	−½	8	0	−½	½
9	½	0	½	10	½	0	−½
11	−½	0	−½	12	−½	0	½
13	½	½	0	14	½	−½	0
15	−½	½	0	16	−½	−½	0
17	−¼	¼	¼	18	¼	−¼	¼
19	¼	¼	−¼	20	−¼	−¼	−¼
21	¼	¼	−¼	22	¼	−¼	¼
23	¼	¼	−¼	24	−¼	−¼	−¼
25	−¼	¼	¼	26	¼	−¼	¼
27	−¼	¼	¼	28	−¼	−¼	−¼

F^{xx}_{xx}, F^{xy}_{xy} and F^{xz}_{xz} are the restoring forces along the three directions for unit displacements of atom 0. The contribution by any atom to each of the above three equations consists of three different terms. The three terms on the right hand side of equation (1) represent the forces produced in the x direction on atom 0, due to displacements of atom i in the x, y or z direction respectively. Similarly the terms on the right hand side of equations (2) and (3) represent the forces along the y and z directions respectively due to x, y and z displacements of atom i. Since the summation is to be carried out over all the 28 neighbours, the three equations contain $(28 \times 9 + 3) = 255$ force components. Actually, however, the number of independent force constants appearing in the equations is reduced considerably by reason of the high degree of symmetry of the crystal. The exact manner in which this reduction is carried out is described below.

It is well known that every crystal by virtue of its symmetry is characterised by a set of symmetry operations which have the property of transforming the entire crystal into itself. In what follows, we shall deal only with symmetry operations which leave the position of atom 0 unchanged. This restriction is essential because we are concerned here with the forces produced at the point 0 due to displacements of the neighbouring atoms. Any symmetry operation can now result only in the interchange among themselves of the individual groups of atoms (4, 12 and 12) which are equidistant from 0. All the atoms of each such group belong to one or the other of the two interpenetrating lattices of carbon atoms. It is also easy to see that digonal rotations about the three cubic axes passing through 0 and reflections in the

six planes of symmetry containing atom 0 and belonging to the tetrahedral group of operations, are sufficient to enable us to bring into coincidence any atom of a particular group with any other atom of the same group.

In the general case of interaction between any two atoms, there will be nine force-components as mentioned above, because corresponding to each one of the three displacements of one of the atoms, there will be a component of the force produced along all the three directions on the second atom. In order to illustrate the manner in which some of the force-components transform among themselves, we shall associate every one of the neighbouring atoms of 0 with three vectors F_{xi}, F_{yi} and F_{zi} corresponding to the three displacements, and the atom 0 with three vectors F^{xo}, F^{yo} and F^{zo} corresponding to the directions of the force components. Every force component will then be connected with two vectors, one corresponding to the direction of the force component on atom 0 and the other corresponding to the direction of displacement of the atom producing the force. For example, the force component F^{yo}_{zi} is associated with the two vectors F^{yo} and F_{zi}. If, by the application of a symmetry operation, the two vectors associated with a force component due to an atom i are transformed into the two vectors associated with a force component due to another atom j, then the magnitudes of the two force components will be the same. For instance, if the two vectors F^{yo} and F_{zi} are transformed respectively into F^{zo} and F_{xj}, then $F^{yo}_{zi} = F^{zo}_{xj}$ (in magnitude only). The two components have the same sign if by the application of the particular operation, the signs of both the vectors associated with one of the force components remain the same and also when both of them are reversed. If however, the sign of one of the vectors is reversed while the sign of the other remains the same, then the two force components will be of opposite sign. In this manner we can determine the relative signs of the force components due to a particular group of atoms. In order to fix the absolute signs of the components with respect to our co-ordinate system, we can consider those components having both their vectors along the positive directions or both along the negative directions of the co-ordinate system, to be negative. Obviously then, the force on any atom P which is proportional to its own displacement, for which the directions of the displacement and of the force are opposite will be positive.

In the case of diamond we find that in addition to the force P, the forces due to the displacements of the nearest neighbours of any atom can be represented by two constants Q and R, of the next-nearest neighbours by five constants S, T, U, V and W, and of the atoms 19 to 28 by five constants α, β, γ, δ and ϵ. A description of the 255 force-components appearing in the three equations (1), (2) and (3) is contained in Tables III, IV and V.

TABLE III

Force-components acting in the x-direction on atom 0

Symbol	Atoms responsible for the forces, the directions of their displacements being				
	x	y	$-y$	z	$-z$
P ..	0	..	..	..	..
Q ..	1 to 4	..	..	..	..
R ..	..	1, 4	2, 3	1, 3	2, 4
S ..	5 to 8	..	..	..	..
T ..	..	5, 8	6, 7	5, 7	6, 8
U ..	9 to 16	..	..	..	..
V ..	..	9, 12	10, 11	13, 15	14, 16
W ..	..	13, 16	14, 15	9, 11	10, 12
α ..	18, 19, 21, 22, 24, 25, 27, 28	..	..	..	..
β ..	..	18, 27	21, 24	19, 25	22, 28
γ ..	..	19, 28	22, 25	18, 24	21, 27
δ ..	17, 20 23, 26	..	..	..	..
ϵ ..	..	17, 26	20, 23	17, 23	20, 26

The exact manner in which the force-components are reduced to 13 independent constants can be understood from these tables. Table III for example, describes the force-components acting on atom 0 due to all possible displacements of the 29 atoms capable of producing a force on atom O in the x-direction. The symbol at the head of each column in Table III denotes the direction of displacements of the atoms which result in a force-component along the positive direction of the x-axis on atom 0. The symbol at the head of each row denotes the magnitude of the force per unit displacement. If we take for instance atom 12, the three X components of force on atom 0 due to x, y and z displacements of the former along the positive directions of the axes are:—

$$F^{x_0}_{x12} = U,\ F^{x_0}_{y12} = V \text{ and } F^{x_0}_{z12} = -W$$

The negative sign occurs in the last equation because it is seen from Table III that the z-displacement vector of atom 12 is negative. Thus Table III

TABLE IV

Force-components acting in the y-direction on atom 0

Symbol	Atoms responsible for the forces, the directions of their displacements being				
	x	$-x$	y	z	$-z$
P ..	..	..	0	..	..
Q ..	..	..	1 to 4	..	..
R ..	1, 4	2, 3	..	1, 2	3, 4
S ..	..	..	9 to 12	..	..
T ..	9, 12	10, 11	..	9, 10	11, 12
U ..	..	..	5 to 8 & 13 to 16	..	..
V ..	5, 8	6, 7	..	13, 14	15, 16
W ..	13, 16	14, 15	..	5, 6	7, 8
α ..	..	..	17, 19, 20, 22, 23, 25, 26, 28,	..	..
β ..	17 26	20, 23	..	19, 22	25, 28
γ ..	19, 28	22, 25	..	17, 20	23, 26
δ ..	..	..	18, 21, 24, 27	..	..
ϵ ..	18, 27	21, 24	..	18 21	24, 27

directly gives us the values of the 85 x-components, Table IV the 85 y-components and Table V the 85 z-components of force acting on atom 0. The 255 force-components being known, we can at once write down the equations of motion of any normal mode of vibration, by substituting the proper displacements of the various atoms (taking care to insert the correct signs) involved in the particular normal mode.

4. THE EXPRESSIONS FOR THE FREQUENCIES OF VIBRATION

In order to express the frequencies of vibration of the different normal modes in terms of the force constants, it is necessary to substitute the displacements of the different atoms from the equilibrium configuration in any particular normal mode, in the three equations 1, 2 and 3 and solve them for the frequency. It should be borne in mind that the x, y and z displacements of any atom are numerically equal to the corresponding displacements of every other atom in the structure. The method of solution can be best

TABLE V

Force-components acting in the z-direction on atom 0

Symbol	Atoms responsible for the forces, the directions of their displacements being				
	x	$-x$	y	$-y$	z
P ..	..	..	..	..	0
Q ..	..	..	..	..	1 to 4
R ..	1, 3	2, 4	1, 2	3, 4	..
S ..	..	..	..	..	13 to 16
T ..	13, 15	14, 16	13, 14	15, 16	..
U ..	..	..	..	..	5 to 12
V ..	5, 7	6, 8	9, 10	11, 12	..
W ..	9, 11	10, 12	5, 6	7, 8	..
α ..	..	..	..	..	17, 18, 20, 21, 23, 24, 26, 27
β ..	17, 23	20, 26	18, 21	24, 27	..
γ ..	18, 24	21, 27	17, 20	23, 26	..
δ ..	..	..	..	..	19, 22, 25, 28
ϵ ..	19, 25	22, 28	19, 22	25, 28	..

explained by illustrating it with a particular case. In mode 2 of Table I representing the tangential motion of the octahedral planes of atoms, if we assume the motion to be in the yz plane, then the x displacements of all the atoms are zero. The y displacements are given by

$$y = y_1 = y_7 = y_8 = y_{10} = y_{12} = y_{14} = y_{15} = y_{20} \text{ to } y_{28}$$
$$= -y_2 \text{ to } -y_6 = -y_9 = -y_{11} = -y_{13} = -y_{16} = -y_{17} \text{ to } -y_{19}$$

and the z displacements are given by $z_i = ky_i$, k being an arbitrary constant.

Equation 1 becomes zero, while 2 and 3 are reduced to

$$m\frac{d^2y}{dt^2} = (\mathrm{P} - 2\mathrm{Q} + 2k\mathrm{R} - 4k\mathrm{W} + 4\alpha - 2k\beta - 2k\gamma + 2\delta - 2k\epsilon)\, y \quad (4)$$

$$km\frac{d^2y}{dt^2} = (k\mathrm{P} + 2k\mathrm{Q} + 2\mathrm{R} - 4\mathrm{W} + 4k\alpha - 2\beta - 2\gamma + 2k\delta - 2\epsilon)\, y \quad (5)$$

On subtracting (5) from (4) the constant k vanishes, showing that the frequency is the same for all values of k including our particular value ($k = -1$) and we get

$$m\frac{d^2y}{dt^2} = y\{P - 2Q - 2R + 4W + 2(2\alpha + \delta) + 2(\beta + \gamma + \epsilon)\} \qquad (6)$$

The frequency of vibration is therefore given by

$$4\pi^2\nu^2c^2m = (P - 2Q - 2R + 4W + 6\Sigma + 6\Omega) \qquad (7)$$

where $\Sigma = \frac{1}{3}(2\alpha + \delta)$ and $\Omega = \frac{1}{3}(\beta + \gamma + \epsilon)$ and ν and c are respectively the frequency in wavenumbers and the velocity of light. In a similar manner, the expressions for all the modes can be obtained easily and are contained in column 6 of Table I. Table I also contains a detailed description of all the modes in columns 2 to 5. There is however an ambiguity with regard to the description of the relative phases of nearest layers in the case of the modes III and VIII. The ambiguity arises because the cubic planes of atoms in diamond are arranged at equal intervals. This fact does not make any difference with regard to the description of modes V and VI because the expressions for the frequencies of these two modes are the same. The ambiguity in the case of III and VIII can be cleared up if we consider any two neighbouring layers for which the phases of motion are the same, and then describe the direction of motion in the two cases, with respect to the plane of the valence bonds joining the two layers. In such a case the direction of motion in III will be perpendicular to the plane of the bonds and in VIII parallel to the plane.

It will be noticed that the constants T and V do not appear in any of the equations. These represent two of the three transverse force-constants due to the displacements of the twelve next-nearest neighbours previously described as situated at the face centres of the twelve cube faces originating from the point 0. Owing to the nature of the displacements of these atoms in the various normal modes, they cancel out from the frequency formulæ.

5. The Force Constants

In addition to the eight expressions for the frequencies of vibration of the various modes, we can obtain one more relation between the constants which corresponds to the translation of the entire crystal having zero frequency. Substituting the values of the force components appearing in equations 4, 5 or 6, we obtain for the case of diamond

$$(P + 4Q + 4S + 8U + 12\Sigma) = 0 \qquad (8)$$

We have now got nine expressions involving the eight constants P, Q, R, S, U, W, Σ and Ω. The constants are therefore perfectly determinate if

the frequencies corresponding to each one of the different modes are taken from the results of the experimental investigations on the vibration spectrum of diamond. The identification of the frequencies contained in column 8 of Table I with the different modes has been carried out with the help of the sequence contained in the same table. The two low frequencies appearing as the last two in Table I have not been measured very accurately. But, a combination of these two has been found to occur at about 1370 cm.$^{-1}$ in infra-red absorption and in luminescence and absorption at low temperatures in the visible region. The eight constants appearing in the equations have therefore been determined by u sing the values of the six accurately known frequencies and the fact that the sum of the low frequencies is at about 1370 cm.$^{-1}$ The values of the constants obtained are contained in Table VI.

TABLE VI

Numerical values of the force-constants $\times 10^{-5}$ *dynes per cm.*

Atom 0	Atoms 1 to 4		Atoms 5 to 16			Atoms 17 to 28	
P	Q	R	S	U	W	Σ	Ω
7·85	−1·39	−0·858	−0·005	−0·131	−0·114	−0·06	+0·005

The fourth, fifth and sixth columns of Table VII show the frequencies calculated from abbreviated formulæ containing only the force constants

TABLE VII

Calculated values of the frequencies

Sequence	Degeneracy	Operative Force-constant	Frequencies from abbreviated formulæ			Complete Formulæ
			P only	P, Q, R	P, Q, R S, U, W	
			cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$	cm.$^{-1}$
I	3	$P-4Q+4S+8U-12\Sigma$	1020	1351	1294	1332
II	8	$P-2Q-2R+4W+6\Sigma+6\Omega$	1020	1294	1269	1250
III	6	$P-4R-4S-12\Omega$	1020	1234	1236	1232
IV	4	$P+2Q-4R-8W-6\Sigma+12\Omega$	1020	1064	1123	1149
V & VI	3+3	$P+4S-8U$	1020	1020	1088	1088
VII	4	$P-2Q+4R-8W+6\Sigma-12\Omega$	1020	973	1038	1008
VIII	6	$P+4R-4S+12\Omega$	1020	744	746	752
IX	8	$P+2Q+2R+4W-6\Sigma-6\Omega$	1020	635	582	620

shown, the number of neighbouring atoms taken into account being respectively 0, 4 and 16. The last column gives the experimentally observed

values which are also those given by the complete expressions taking all the force constants for the 28 neighbouring atoms into account. The values of the constants assumed are in every case those shown in Table VI.

It will be noticed from Table VI that P, Q and R are numerically by far the largest constants, as is to be expected since the four nearest atoms are linked directly by valence bonds to the atom under consideration, while the other atoms are only indirectly connected with it. Further, all the constants except P and Ω are seen to be negative. This could have been foreseen from equation (8), since P being taken as positive, then by the nature of the case the quantities Q, S, U and Σ should be negative, while the constants R and W come out negative by reason of the convention adopted regarding their sign. Table VI further shows that P is greater than 4Q, as could also have been foreseen from relation (8). The constant S comes out as practically negligible, and this is not surprising since it represents the forces on any atom due to others situated in the same cubic plane but not directly linked with it, the direction of both force and displacement being normal to the plane.

Column 5 of Table VII shows that the three constants P, Q, R suffice to give a tolerable fit with the experimentally observed values. The relative values of P, Q and R determine the sequence of the frequencies calculated from the formulæ, and this is the same as that of the observed frequencies provided that numerically $2R > Q > R$, as is actually the case. That Q would be numerically greater than R could have been expected since the former is the longitudinal and the latter the transverse component of the force exerted by one atom on another linked to it by a valence bond. If $2R < Q$, mode IV would have a lower frequency than mode VII which would scarcely have been possible in view of the much larger bond-length variations involved in the former mode.

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Summary

Exact expressions have been derived for the frequencies of the nine normal modes of vibration of the diamond structure, which take account of the forces of interaction between each atom and its 28 nearest neighbours. The formulæ involve 8 independent constants together with an additional relation between them, and the constants are thus perfectly determinate

if the frequencies are known. The interactions decrease very rapidly with the increase of distance and their magnitudes and directions as evaluated from the observed frequencies are also otherwise in accord with theoretical expectations.

References

1. Bhagavantam, S. .. *Proc. Ind. Acad. Sci.*, A, 1943, **18**, 251.
2. Chelam, E. V. .. *Ibid.*, 1943, **18**, 334.
3. Nagendra Nath, N. S. .. *Ibid.*, 1934, **1**, 333.
4. Raman, C. V. .. *Ibid.*, 1943, **18**, 237.
5. Ramanathan, K. G. .. *Ibid.*, 1946, **24**, 150.
6. ———— .. *Ibid.*, 1947, **26**, 469.

DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part II. The Rocksalt Structure

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1. Introduction

Many solids crystallise with a structure similar to that of rocksalt and it is therefore of importance to investigate the vibration spectrum of this crystal. Expressions for the frequencies of its nine eigenvibrations are derived in this paper by methods similar to those adopted in the case of diamond in the preceding communication.

2. Description of the Modes

As in the case of diamond, the modes of vibration of the rocksalt structure can be derived directly from the four possible modes of vibration of the face-centred cubic lattice, *viz.*, the normal and tangential oscillations of the octahedral planes of atoms and the normal and tangential oscillations of the cubic planes of atoms with degeneracies of 4, 8, 3 and 6 respectively. Since there are two atoms per unit cell in rocksalt, the number of possibilities is doubled up just as in diamond. The atoms in any particular cell can move either with the same phase or with opposite phases in every one of the four possibilities of a simple face-centred lattice. But, the case of rocksalt differs from diamond in some important respects. Firstly, the two atoms in the unit cell have different masses. Secondly, while in diamond, the layers of atoms belonging to the two interpenetrating lattices appear separated both in the octahedral and in the cubic planes, in rocksalt the layers are separated only in the octahedral planes, the cubic planes consisting of atoms of both kinds located in the same layer. Further, the octahedral layers are spaced at equal intervals, any layer of atoms of one kind being situated exactly midway between neighbouring layers of the other kind. Because of this, the equations of motion of the two types of atoms for the four octahedral modes are independent of each other. These modes are the normal and tangential oscillations of the octahedral layers of sodium atoms and the normal and tangential oscillations of the octahedral layers of chlorine atoms

having degeneracies of 4, 8, 4 and 8 respectively. In the case of the modes in which the cubic planes are involved, the equations of motion of the two types of atoms are not independent of each other for the reason stated above. There will be two modes in which the planes move normally with respect to themselves. In one of these, the atoms belonging to the two lattices situated in any cubic plane move with the same phase and in the other with opposite phases. The degeneracies for these two modes are three each. Similarly, corresponding to the above two possibilities, there will be two tangential modes with degeneracies of 6 each. In addition to the eight modes described already, there will be one more triply degenerate mode in which the atoms belonging to the two lattices move against each other in any three orthogonal directions.

3. The Force-Constants

In the discussion below, we shall deal with the forces produced on any sodium atom proportional to its own displacement and those due to the displacements of the 26 atoms nearest to itself. Similarly we shall have to consider also the forces produced on any chlorine atom due to its own displacement and the displacements of its 26 nearest neighbours. There will therefore be $2(26 \times 9 + 3) = 474$ force-components in all. The 26 neighbours of any atom (sodium or chlorine) are situated in such a manner that if we consider any unit cube of the crystal with the atom under consideration at the centre of the cube, then the six atoms (of the other kind, 1 to 6) situated at the face-centres of the cube are the nearest neighbours. The twelve atoms (7 to 18 of the same kind) located at the midpoints of the 12 cube edges and the eight atoms (19 to 26 of the other kind) situated at the eight corners of the cube form the next nearest and the more distant neighbours respectively. The 474 force-components mentioned above, would be greatly reduced in number for various reasons. There are actually three different factors which contribute to such reduction. Firstly, the 26 neighbours divide themselves into three different groups of atoms of 6, 12 and 8 such that the forces on the atom under consideration due to the displacements of all the atoms of a particular species can be described by the same set of constants. Secondly, the forces produced on any atom of one kind (say chlorine) due to the displacements of any other atom of the second kind, are the same as the forces produced by the displacements of the particular atom of the first kind on the same atom of the second kind. Thirdly, symmetry effects a great simplification and reduction of the number of independent constants. In addition to the fact that the force constants of different atoms of a particular group transform among themselves, it may also happen that some of the constants

vanish. If by the application of a symmetry operation, the force in a particular direction on any atom (i) due to the displacements of another atom (j) in a particular direction comes out to be equal to the force on the same atom, (i) in the same direction by the displacement of (j) in the opposite direction then the force must vanish. Applying these principles, we find that the 474 force components can be reduced to 12 independent constants. A description of all the force constants is contained in Table I.

TABLE I

(See Explanatory note below)

Atoms responsible for forces	Symbol	Description of Force-Constants
0	P, P′	Force on atom proportional to its own displacement.
1 to 6	Q	Force and displacement parallel to each other and to the line joining the two atoms.
1 to 6	R	Force and displacement perpendicular to the cubic plane containing the two atoms.
7 to 18	S, S′	Force and displacement perpendicular to the cubic plane containing the two atoms.
7 to 18	T, T′	Force and displacement along the same cube axis, the plane containing the two being the cubic plane containing the two atoms.
7 to 18	U, U′	Force and displacement along different cube axes, the plane containing the two being the cubic plane containing the two atoms.
19 to 26	V	Directions of both force and displacement along a cube axis.
19 to 26	W	Direction of displacement along a cube axis and that of the force along any one of the other two axes.

Atom 0 may refer to either sodium or chlorine and the other numbers accordingly. The symbols P, S, T and U refer to sodium atoms and P′, S′, T′ and U′ to chlorine atoms. The other symbols Q, R, V and W are common to both.

In addition to the simplifications already described, we can derive two relations between the force constants, one representing the fact that the work done in any small displacement (δx) of the entire crystal is zero and the other that the work done in any small displacement (δx) of all the chlorine atoms is exactly equal to the work done in an equal displacement of all the sodium atoms, the chlorines now remaining at rest. These two relations are :

$$\{(P+2Q+4R+4S+8T+8V) + (P'+2Q+4R+4S'+8T'+8V)\}\,\delta x^2=0 \quad (1)$$

and $$(P+4S+8T)\,\delta x^2 = (P'+4S'+8T')\,\delta x^2 \quad (2)$$

combining (1) and (2), we find that

$$(P+4S+8T) = (P'+4S'+8T') = -(2Q+4R+8V) \quad (3)$$

4. The Frequency Expressions

We will now proceed to derive expressions for the frequencies of vibration of the nine modes. In what follows, the masses of the sodium and chlorine atoms will be represented by m_1 and m_2 and their displacements by $x_1 y_1 z_1$ and $x_2 y_2 z_2$ respectively. The x, y and z displacements of any sodium atom in a particular normal mode will be numerically the same as the corresponding displacements of any other sodium atom, the directions of displacement being defined by the normal mode. Similarly the numerical values of the displacements will be the same for all the chlorine atoms. The deduction of the equations of motion of the various normal modes has not been shown here in detail as they can be written out in all the cases by mere inspection of a model.

A: The two lattices oscillating against each other in any three orthogonal directions. At any instant of time the two types of ions will be moving in opposite directions. The direction of motion in this case can be anything. So let us put $y = ax$ and $z = bx$; the constants (a) and (b) depending on the direction of displacement. The equations of motion involving x will be

$$\left.\begin{aligned} m_1 \frac{d^2x_1}{dt^2} &= (\mathrm{P} + 4\mathrm{S} + 8\mathrm{T})\, x_1 - (2\mathrm{Q} + 4\mathrm{R} + 8\mathrm{V})\, x_2 \\ m_2 \frac{d^2x_2}{dt^2} &= -(2\mathrm{Q} + 4\mathrm{R} + 8\mathrm{V})\, x_1 + (\mathrm{P}' + 4\mathrm{S}' + 8\mathrm{T}')\, x_2 \end{aligned}\right\} \quad (4)$$

The y and z equations of motion will be quite similar to these two. The constants (a) and (b) do not enter the equations, showing that the frequency of vibration is independent of the direction of motion. Denoting the expression $\left(\frac{1}{m_1} + \frac{1}{m_2}\right)$ by $1/\mu$, the two equations (4) lead to the solution

$$4\pi^2 c^2 \nu_1^2 \mu =$$

$$(\mathrm{P} + 4\mathrm{S} + 8\mathrm{T}) = (\mathrm{P}' + 4\mathrm{S}' + 8\mathrm{T}') = -(2\mathrm{Q} + 4\mathrm{R} + 8\mathrm{V})$$

B: Oscillation of the alternate octahedral layers of sodium atoms against each other normally with respect to themselves. In this case the displacements of the chlorine atoms will be zero. If we assume the (111) planes to be the oscillating units $x = y = z$. The equation of motion for x becomes

$$m_1 \frac{d^2x_1}{dt^2} = (\mathrm{P} - 8\mathrm{U})\, x_1 \quad (5)$$

with two identical equations for y_1 and z_1. Therefore

$$4\pi^2 c^2 \nu_2^2 m_1 = (\mathrm{P} - 8\mathrm{U}).$$

C: Oscillation of the alternate octahedral layers of sodium atoms against each other tangentially with respect to themselves. The direction of motion can be anywhere in the plane, since the vibration is degenerate in the plane. Also the equation of motion comes out to be the same whatever the direction of motion, provided it is confined to the octahedral plane under consideration. If we suppose the direction of motion to be along any one of the three dodecahedral directions lying in the plane, for example $x = 0$ and $y = -z$, then

$$\left.\begin{aligned} m_1 \frac{d^2y_1}{dt^2} &= (\mathrm{P} + 4\mathrm{U})\, y_1 \\ \text{and} \qquad m_1 \frac{d^2z_1}{dt^2} &= (\mathrm{P} + 4\mathrm{U})\, z_1 \end{aligned}\right\} \qquad (6)$$

Hence $$4\pi^2 c^2 \nu_3^2 m_1 = (\mathrm{P} + 4\mathrm{U})$$

D: Similarly the frequencies of vibration of the normal and tangential oscillations of the alternate octahedral layers of chlorine atoms come out as

$$4\pi^2 \nu_4^2 c^2 m_2 = (\mathrm{P}' - 8\mathrm{U}')$$

and $$4\pi^2 \nu_5^2 c^2 m_2 = (\mathrm{P}' + 4\mathrm{U}').$$

E: Coupled oscillation of the alternate cubic planes of atoms normally to each other. The direction of displacement can be along any one of the three cube axes. Let y and z be zero. Then, there are two possibilities corresponding to whether the sodium and chlorine atoms in any particular YZ plane move with the same phase or with opposite phases. When these displacements are in the same phase

$$\left.\begin{aligned} m_1 \frac{d^2x_1}{dt^2} &= (\mathrm{P} + 4\mathrm{S} - 8\mathrm{T})\, x_1 - (2\mathrm{Q} - 4\mathrm{R} + 8\mathrm{V})\, x_2 \\ m_2 \frac{d^2x_2}{dt^2} &= -(2\mathrm{Q} - 4\mathrm{R} + 8\mathrm{V})\, x_1 + (\mathrm{P}' + 4\mathrm{S}' - 8\mathrm{T}')\, x_2 \end{aligned}\right\} \qquad (7)$$

The frequencies ν_6 and ν_7 are therefore given by

$$4\pi^2 c^2 \nu_6^2 \text{ and } 4\pi^2 c^2 \nu_7^2$$

$$= \frac{\mathrm{P} + 4\mathrm{S} - 8\mathrm{T})}{2m_1} + \frac{\mathrm{P}' + 4\mathrm{S}' - 8\mathrm{T}'}{2m_2}$$

$$\pm \left\{ \left[\frac{\mathrm{P} + 4\mathrm{S} - 8\mathrm{T}}{2m_1} - \frac{\mathrm{P}' + 4\mathrm{S}' - 8\mathrm{T}'}{2m_2} \right]^2 + \frac{(2\mathrm{Q} - 4\mathrm{R} + 8\mathrm{V})^2}{m_1 m_2} \right\}^{\frac{1}{2}}$$

The case in which the sodium and chlorine atoms of any YZ plane move with opposite phases also leads to the same two solutions. The + *ive* sign refers to the case in which the sodium and chlorine atoms of any YZ plane move

with the same phase and the — *ive* sign to the case in which they move with opposite phases.

F: Coupled oscillation of the alternate cubic planes of atoms tangentially to themselves. Here again if we consider the YZ planes as the oscillating units, the direction of motion can be anywhere in the plane. But, the y and z equations of motion come out to be identical. When the motion of sodium and chlorine atoms are in phase

$$\left.\begin{aligned} m_1 \frac{d^2y_1}{dt^2} &= (\mathrm{P} - 4\mathrm{S})\, y_1 + (2\mathrm{Q} - 8\mathrm{V})\, y_2 \\ m_2 \frac{d^2y_2}{dt^2} &= (2\mathrm{Q} - 8\mathrm{V})\, y_1 + (\mathrm{P}' - 4\mathrm{S}')\, y_2 \end{aligned}\right\} \qquad (8)$$

Therefore ν_8 and ν_9 are given by

$$4\pi^2c^2\nu_8^2 \text{ and } 4\pi^2c^2\nu_9^2$$
$$= \frac{\mathrm{P} - 4\mathrm{S}}{2m_1} + \frac{\mathrm{P}' - 4\mathrm{S}'}{2m_2}$$
$$\pm \left\{\left[\frac{\mathrm{P} - 4\mathrm{S}}{2m_1} - \frac{\mathrm{P}' - 4\mathrm{S}'}{2m_2}\right]^2 + \frac{(2\mathrm{Q} - 8\mathrm{V})^2}{m_1 m_2}\right\}^{\frac{1}{2}}$$

TABLE II

The Expressions for the Frequencies of Vibration of the Normal Modes of NaCl type Structures

Degeneracy	Oscillating units	Direction of Oscillation	$4\pi^2c^2\nu^2$
3	The two lattices	Arbitrary	$(\mathrm{P}+4\mathrm{S}+8\mathrm{T})/\mu = (\mathrm{P}'+4\mathrm{S}'+8\mathrm{T}')/\mu' = -(2\mathrm{Q}+4\mathrm{R}+8\mathrm{V}/\mu$
4	(111) Na ions	Normal	$(\mathrm{P}-8\mathrm{U})/m_1$
8	,,	Tangential	$(\mathrm{P}+4\mathrm{U})/m_1$
4	(111) Cl ions	Normal	$(\mathrm{P}'-8\mathrm{U}')/m_2$
8	,,	Tangential	$(\mathrm{P}'+4\mathrm{U}')/m_2$
3	(100) planes	Normal	$\frac{\mathrm{P}+4\mathrm{S}-8\mathrm{T}}{2m_1} + \frac{\mathrm{P}'+4\mathrm{S}'-8\mathrm{T}'}{2m_2} \pm \left\{\left[\frac{(\mathrm{P}+4\mathrm{S}-8\mathrm{T})}{2m_1} - \frac{(\mathrm{P}'+4\mathrm{S}'-8\mathrm{T}')}{2m_2}\right]^2 + \frac{(2\mathrm{Q}-4\mathrm{R}+8\mathrm{V})^2}{m_1m_2}\right\}^{\frac{1}{2}}$
3	,,	Normal	
6	,,	Tangential	$\frac{\mathrm{P}-4\mathrm{S}}{2m_1} + \frac{\mathrm{P}'-4\mathrm{S}'}{2m_2} \pm \left\{\left[\frac{\mathrm{P}-4\mathrm{S}}{2m_1} - \frac{\mathrm{P}'-4\mathrm{S}'}{2m_2}\right]^2 + \frac{(2\mathrm{Q}-8\mathrm{V})^2}{m_1m_2}\right\}^{\frac{1}{2}}$
6	,,	Tangential	

As in the case of the modes ν_6 and ν_7, here also the mode in which the sodiums and chlorines of any one plane move in opposite phases leads to the same two solutions. In this case, the mode with which the motions are in the same phase corresponds to the $-$ *ive* sign and the $+$ *ive* sign to the mode in which the phases of sodium and chlorine atoms in any oscillating plane, are opposite. Finally, we give a table containing all the expressions collected together with a description of the various modes of vibration.

In conclusion the author's sincere thanks are due to Prof. Sir C. V. Raman for the many illuminating discussions he had with him.

Summary

Exact expressions for the frequencies of the nine eigenvibrations of rocksalt have been derived in terms of 11 independent constants which take account of the influence of the 26 nearest neighbours of each atom, the constants being connected by two additional relations.

DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part III. The Cæsium Chloride Structure

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction

In two previous communications the vibration spectra of diamond and rocksalt have been investigated on the basis of the new theory of crystal dynamics (1943). It is proposed here to deal with the dynamics of the cæsium chloride structure which is typical of a number of crystals. The same method as was used in the two previous publications has been applied in the present case also.

2. The Normal Modes of Vibration

Since the cæsium chloride structure consists of two simple cubic lattices interpenetrating in such a manner that the atoms of one lattice are located at the body centres of the cubic lattice formed by the other, the normal modes of vibration of this structure are easily derived by a consideration of the vibration modes of a simple cubic lattice. Of the five independent modes of vibration possible for a simple cubic lattice, two are the normal and tangential oscillations of the alternate cubic planes of atoms against each other with degeneracies of 3 and 6 respectively. Modes three and four with degeneracies of 3 and 6 respectively, are the oscillations of the alternate dodecahedral planes of atoms against each other, the directions of oscillation being along the cubic axis lying in the dodecahedral plane in one case and along any one of the two dodecahedral axis lying in the perpendicular plane in the other. The fifth mode is the oscillation of the alternate octahedral planes of atoms with opposite phases in any three orthogonal directions and consequently with degeneracy of 3, thus making up the 21 degrees of freedom of the 8 atoms in a supercell, besides the three translations. In the case of the cæsium chloride structure, since the two non-equivalent atoms in a unit cell can now vibrate with either the same phase or with opposite phases, the five possibilities in the simple cubic lattice will be doubled up. In addition to the 10 independent modes thus possible, there will be one

other in which the atoms belonging to the two lattices vibrate against each other in any three orthogonal directions. A symbolic description of these eleven modes of vibration is contained in columns 1 to 3 of Table II. To avoid repetition, it is not reproduced here.

The cæsium and chlorine atoms in the crystal appear in separate layers parallel to the octahedral and cubic planes of the crystal and they are so spaced that the layers of atoms of one lattice are situated midway between layers belonging to the other lattice both in the octahedral and in the cubic planes. Therefore the equations of motion of the two types of atoms are independent so far as the modes concerned are the vibrations of the cubic or octahedral planes. But any dodecahedral layer contains atoms of both types and consequently for the modes in which these layers are involved, the equations for the two types of atoms are not independent.

3. The Force Constants

In what follows we shall consider the forces produced on every atom due to the displacements of the 26 neighbouring atoms in addition to the forces due to its own displacements. Since there are two dissimilar atoms in the crystal, we would require $2(26 \times 9 + 3) = 474$ force-components to describe the influence of the neighbouring atoms. But, for reasons already described in the previous paper, these reduce very much in number. In the case of cæsium chloride the eight nearest neighbours (of the other kind) of every atom, are situated at the eight corners of the unit cube, the atom under consideration being situated at the body centre of the cube. If we consider a cube of twice the linear dimensions of the unit cube with the atom under consideration again situated at the body centre, then the six next nearest neighbours (9 to 14 of the same kind) are those at the face centres of the big cube and the most distant of the 26 atoms (15 to 26 of the same kind) at the midpoints of the 12 cube edges of the big cube. The constants P and P′ refer to the forces on any cæsium or chlorine atom (atom 0) respectively proportional to their own displacements. Atoms 1 to 8 are represented by Q and R, 9 to 14 by S, T, S′ and T′ and 15 to 26 by U, V, W and U′, V′, W′. The description of these thirteen constants is contained in Table I.

As in the case of rocksalt, the principle that an infinitesimal translation of the entire crystal involves no work done and the fact that the work done in a small virtual displacement of the cæsium ions by a small amount δx is exactly equal to the work done in a displacement of the chlorine ions by the same amount, the cæsiums now remaining at rest lead to the relations

$$\{(P+8Q+4S+2T+4U+8V) + (P'+8Q+4S'+2T'+4U'+8V')\}\,\delta x^2=0 \quad (1)$$

TABLE I

Description of Force Constants

Atoms responsible for forces	Symbol	Description of the constant
0	P, P'	Force on any atom proportional to its own displacement along any one of the cube axes
1 to 8	Q	Direction of both force and displacement along any one of the three cube axes
do	R	Direction of displacement along a cube axis and that of force along any one of the other two cube axes
9 to 14	S, S'	Both force and displacement in a direction perpendicular to the cubic plane containing the two atoms
do	T, T'	Both force and displacement along a cubic axis containing the two atoms
15 to 26	U, U'	Both force and displacement in a direction perpendicular to the cubic plane containing the two atoms
do	V, V'	Direction of both force and displacement along any one of the three cube axes
do	W, W'	Direction of displacement along a cube axis and that of force along any one of the other two cube axes

* Atom O may refer to either a Cæsium atom or a Chlorine atom. P, S, T, U and W refer to cæsium atoms, P', S', T', U' and W' to chlorine atoms and Q and R to both.

and

$$(P+4S+2T+4U+8V)\,\delta x^2 = (P'+4S'+2T'+4U'+8V')\,\delta x^2 \qquad (2)$$

combining (1) and (2) we obtain

$$(P+4S+2T+4U+8V) = (P'+4S'+2T'+4U'+8V') = -(8Q) \qquad (3)$$

4. EXPRESSIONS FOR THE FREQUENCIES

We shall now consider the eleven normal modes one by one and derive the frequency formulæ in terms of the force-constants. m_1 and m_2 denote the masses of the cæsium and chlorine atoms respectively.

A: The oscillation of the cæsium and chlorine lattices against each other along any three orthogonal directions. If we represent the displacements of any cæsium atom by $x_1\, y_1\, z_1$ and that of the chlorine atoms by $x_2\, y_2\, z_2$ we have

$$m_1 \frac{d^2(x_1+y_1+z_1)}{dt^2} = (P+4S+2T+4U+8V)(x_1+y_1+z_1) - 8Q(x_2+y_2+z_2)$$

$$m_2 \frac{d^2(x_2+y_2+z_2)}{dt^2} = -8Q(x_1+y_1+z_1) + (P'+4S'+2T'+4U'+8V')(x_2+y_2+z_2).$$

Using the relation (3) and solving the above two equations we obtain

$$4\pi^2\nu_1^2c^2 = (P + 4S + 2T + 4U + 8V)/\mu$$
$$= (P' + 4S' + 2T' + 4U' + 8V')/\mu = -(8Q)/\mu.$$

μ in the above is the reduced mass of the cæsium and chlorine atoms

$$1/\mu = (1/m_1 + 1/m_2)$$

B: The cæsium ions in the cubic planes vibrate against each other with alternate planes in opposite phases, normally. If we choose the YZ planes as the oscillating units

$$m_1 \frac{d^2x_1}{dt^2} = (P + 4S + 4U - 2T - 8V)\, x_1$$

The frequency of vibration is therefore

$$4\pi^2\nu_2^2 m_1 c^2 = (P + 4S + 4U - 2T - 8V).$$

C: Same as B but transversely. The direction of oscillation can be anywhere in the plane. Hence

$$m_1 \frac{d^2(y_1 + z_1)}{dt^2} = (P + 2T - 4U)(y_1 + z_1)$$

$$\text{or } 4\pi^2\nu_3^2 m_1 c^2 = P + 2T - 4U.$$

D: Movement of the chlorine layers in the alternate cubic planes against each other normally or transversely. The frequency expressions will be similar to those in B and C but with the dashed terms. Hence

$$4\pi^2\nu_4^2 m_2 c^2 = (P' + 4S' + 4U' - 2T' - 8V')$$
$$4\pi^2\nu_5^2 m_2 c^2 = (P' + 2T' - 4U').$$

E: Coupled oscillation of cæsium and chlorine atoms in alternate dodecahedral planes with opposite phases, the directions of oscillation being along the diagonals of the cube face perpendicular to the oscillating planes: If we consider the (011) planes, then the displacements of the atoms will be such that $x = 0$ and $y = \pm z$. Therefore for the two types of atoms

$$m_1 \frac{d^2y_1}{dt^2} = (P - 2T - 4U)\, y_1 - 8Ry_2$$

$$m_2 \frac{d^2y_2}{dt^2} = -8Ry_1 + (P' - 2T' - 4U')\, y_2.$$

The two frequencies ν_6 and ν_7 are therefore given by $4\pi^2\nu_6^2c^2$, $4\pi^2\nu_7^2c^2 =$

$$\frac{P - 2T - 4U}{2m_1} + \frac{P' - 2T' - 4U'}{2m_2}$$
$$\pm \left\{\left[\frac{P - 2T - 4U}{2m_1} - \frac{P' - 2T' - 4U'}{2m_2}\right]^2 + \frac{(8R)^2}{m_1 m_2}\right\}^{\frac{1}{2}}$$

F: Same as E, but the direction of oscillation being tangential to the dodecahedral plane and along a cube edge. The equations of motion for the (011) planes are

$$m_1 \frac{d^2x_1}{dt^2} = (P - 4S + 2T + 4U - 8V)\, x_1$$

$$m_2 \frac{d^2x_2}{dt^2} = (P' - 4S' + 2T' + 4U' - 8V')\, x_2$$

In this case the equations of motion appear separated because the forces due to the displacements of one set of atoms on any atom of the other set cancel out completely in these two modes. The two frequencies are therefore

$$4\pi^2\nu_8^2 m_1 c^2 = (P - 4S + 2T + 4U - 8V)$$

$$4\pi^2\nu_9^2 m_2 c^2 = (P' - 4S' + 2T' + 4U' - 8V').$$

G: Alternate cæsium layers in the octahedral planes vibrating in opposite phases against each other in any three orthogonal directions. The x, y and z equations of any atom are identical. Therefore

$$m_1 \frac{d^2(x_1 + y_1 + z_1)}{dt^2} = (P - 4S - 2T + 4U + 8V)(x_1 + y_1 + z_1)$$

Hence

$$4\pi^2\nu_{10}^2 m_1 c^2 = (P - 4S - 2T + 4U + 8V).$$

H: Alternate chlorine layers in the octahedral planes vibrating in opposite phases against each other in any three orthogonal directions. The frequency expression for this mode will be quite similar to that of the above

$$4\pi^2\nu_{11}^2 m_2 c^2 = (P' - 4S' - 2T' + 4U' + 8V').$$

Finally, the results are collected together and presented in Table II.

5. Some Further Simplifications

It will be noticed from Table I that the displacements which give rise to the forces S, S', U and U' involve no change in the distance between the interacting atoms. Consequently their magnitudes will be negligibly small in comparison with those of the other constants. The constants W and W' do not appear in any one of the 11 formulæ in Table II. Further, if we neglect V and V' which arise out of the displacements of the most distant neighbours considered, we will be left with the constants P, P', Q, R, T and T' which should satisfy the relation

$$(P + 2T) = (P' + 2T') = -(8Q)$$

Also since by the nature of the forces $P \gg T$ and $P' \gg T'$, it follows that

$$P \approx P'$$

TABLE II

Expressions for the Frequencies of the Normal Modes

Degeneracy	Oscillating Units	Direction of Oscillation	Expression for the frequencies $(4\pi^2\nu^2c^2)$
3	The two lattices	Arbitrary	$(P+4S+2T+4U+8V)/\mu$ $= (P'+4S'+2T'+4U'+8V')/\mu = -(8Q)/\mu$
3	(100) Cs ions	Normal	$(P+4S+4U-2T-8V)/m_1$
6	do	Tangential	$(P+2T-4U)/m_1$
3	(100) Cl ions	Normal	$(P'+4S'+4U'-2T'-8V')/m_2$
6	do	Tangential	$(P'+2T'-4U')/m_2$
6	(011) planes	[011] or	$\frac{P-2T-4U}{2m_1}+\frac{P'-2T'-4U'}{2m_2} \pm$
6	do	[01$\bar{1}$]	$\left\{\left[\frac{P-2T-4U}{2m_1}-\frac{P'-2T'-4U'}{2m_2}\right]^2+\frac{(8R)^2}{m_1m_2}\right\}^{\frac{1}{2}}$
3	do	[100]	$(P-4S+2T+4U-8V)/m_1$
3	do	[100]	$(P'-4S'+2T'+4U'-8V')/m_2$
3	(111) Cs ions	Arbitrary	$(P-4S-2T+4U+8V)/m_1$
3	(111) Cl ions	Arbitrary	$(P'-4S'-2T'+4U'+8V')/m_2$

TABLE III

Serial No.	Degeneracy	Oscillating Units	Direction of Oscillation	Formulæ
I	6	(011) planes	[011] or [01$\bar{1}$]	$\frac{P-2T}{m_1}+\frac{P'-2T'}{m_2}+\frac{4(T+T')}{m_1+m_2}$
II	3	The two lattices	Arbitrary	$\frac{P+2T}{m_1}+\frac{P'+2T'}{m_2}$
III	3	(111) Cl ions	do	$(P'-2T')/m_2$
IV	3	(100) do	Normal	$(P'-2T')/m_2$
V	3	(011) do	[100]	$(P'+2T')/m_2$
VI	6	(100) do	Tangential	$(P'+2T')/m_2$
VII	3	(111) Cs ions	Arbitrary	$(P-2T)/m_1$
VIII	3	(100) do	Normal	$(P-2T)/m_1$
IX	3	(011) do	[100]	$(P+2T)/m_1$
X	6	(100) do	Tangential	$(P+2T)/m_1$
XI	6	(011) planes	[011 or [01$\bar{1}$]	$-\frac{4(T+T')}{m_1+m_2}$

If the nature of the forces are such that they are along the line joining the interacting atoms, then Q and R the longitudinal and transverse forces respectively, due to the displacements of the nearest neighbours, will be equal since they are all situated along the trigonal directions with respect to the atom under consideration. Once these simplifying assumptions are made, the order of magnitudes of the eleven frequencies, at once follows. By the convention adopted, all the constants except P and P′ are negative. The number of distinct frequencies is thus reduced from 11 to 7. In Table III the various modes are arranged in the order of the magnitudes of their frequencies assuming m_1 to be greater than m_2 as in cæsium chloride. If $m_1 < m_2$ as for example in $NH_4^+Cl^-$ which has the same structure, the order can be obtained by interchanging m_1 and m_2 in Table III and also P and T with P′ and T′ respectively.

My sincere thanks are due to Prof. Sir C. V. Raman for the many valuable suggestions I had from him.

Summary

Exact expressions have been derived for the 11 eigenfrequencies of the cæsium chloride structure in terms of 12 constants which take account of the influence of the 26 nearest neighbours of every atom, the constants being connected by two additional relations. Simplified formulæ for the frequencies have also been given in terms of 4 independent constants only, which are again connected by an additional relation.

DYNAMICAL THEORY OF THE VIBRATION SPECTRA OF CRYSTALS

Part IV. The Metallic Crystals

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1. Introduction

Most metals crystallise in the cubic system with either the face-centred or the body-centred structure and consequently it is of importance to investigate the vibration spectra of these structures. The methods of the foregoing papers have therefore been applied here to derive expressions for the frequencies of the eigenvibrations of the above two structures.

2. The Face-centred Cubic Lattice

The vibration spectrum of this structure has already been described as consisting of four independent modes, *viz.*, the normal and tangential oscillations of the octahedral planes of atoms and the normal and tengential oscillations of the cubic planes of atoms with degeneracies of 4, 8, 3 and 6 respectively. The influence of the 12 nearest neighbours (atoms 1 to 12) surrounding every atom in the structure can be represented by three independent force constants Q, R and S and that of the next nearest neighbours (atoms 13 to 18) by two independent constants T and U. The six constants including P, the force on any atom proportional to its own displacement, are described in Table I.

The condition that an infinitesimal translation of the entire structure involves no work done, results in the relation

$$P + 4Q + 8R + 2T + 4U = 0$$

between the force constants. The expressions for the frequencies of the four eigenvibrations are contained in Table II.

From Table I it can be seen that Q and U will be negligible in comparison with the other constants. R and S will be of the same order of magnitude, but $R > S$ in a valence structure, since the former is a longitudinal and the latter a transverse force. It is also evident that $P > (-8R)$. So

TABLE I

Description of the Force Constants

Atoms responsible for forces	Symbol	Description
0	P	Force on any atom proportional to its own displacement
1 to 12	Q	Force and displacement perpendicular to the cubic plane containing the two atoms
1 to 12	R	Force and displacement along the same cubic axis, the plane containing the two being the cubic plane containing the two atoms
1 to 12	S	Force and displacement along different cube axes, the plane containing the two being the cubic plane containing the two atoms
13 to 18	T	Force and displacement parallel to each other and to the line joining the two atoms
13 to 18	U	Force and displacement perpendicular to the cubic plane containing the two atoms

TABLE II

Expressions for the Frequencies of Vibration

Probable Sequence	Degeneracy	Oscillating Units	Direction of oscillation	$4\pi^2\nu^2c^2\ m$
I	3	(100) planes	Normal	P+4Q−8R+2T+4U
II	4	(111) planes	Normal	P−8S−2T−4U
III	6	(100) planes	Tangential	P−4Q+2T+4U
IV	8	(111) planes	Tangential	P+4S−2T−4U

if we neglect the constant T, the order of magnitude of the frequencies will be the same as that shown in Table II. But T being a negative quantity, it is possible that a consideration of this force might bring about a reversal of the order with regard to modes I and II. In any case the vibration spectrum of the face-centred lattice consists of a close doublet with high frequency, one mode with medium frequency and one mode with low frequency.

3. THE BODY-CENTRED CUBIC LATTICE

The vibration spectrum of the body-centred cubic lattice consists of a triply degenerate vibration of the two interpenetrating cubic lattices against each other and three vibrations of alternate dodecahedral planes with opposite phases, in three directions, *viz.*, normally, transversely parallel to

a cube axis, and transversely along the dodecahedral axis in the plane, with degeneracies of 6 each. The interaction of every atom in the structure with its eight nearest neighbours (atoms 1 to 8) can be represented by two constants Q and R and that with the next nearest neighbours by the constants S and T. So we have four independent constants in addition to the force P on any atom proportional to its own displacement. The constants are described in Table III.

TABLE III

Description of Force Constants

Atoms responsible for forces	Symbol	Description
0	P	Force on any atom proportional to its own displacement
1 to 8	Q	Force and displacement parallel to each other and along a cube axis
1 to 8	R	Force and displacement perpendicular to each other and along different cube axes
9 to 14	S	Force and displacement perpendicular to the cubic plane containing the two atoms
9 to 14	T	Force and displacement parallel to each other and to the line joining the two atoms

The condition that a translation of the crystal has zero frequency leads to

$$P + 8Q + 4S + 2T = 0$$

The frequencies of the modes obtained in terms of the constants are contained in Table IV.

TABLE IV

Expressions for the Frequencies of Vibration

Probable Sequence	Degeneracy	Oscillating Units	Direction of oscillation	$4\pi^2\nu^2c^2m$
I	3	Body centre atoms against cube corner atoms	Arbitrary	$P-8Q+2T+4S$
	6			
II		(011) planes	[011]	$P-8R-2T$
III	6	(011) planes	[100]	$P+2T-4S$
IV	6	(011) planes	[01$\bar{1}$]	$P+8R-2T$

In this case the quantity S will be negligible, as can be inferred from its description in Table III. If we further neglect T, then $P = -(8Q)$ and also

$Q > R$ for the reason that the former is a longitudinal force and the latter a transverse force, the directions of the line joining the interacting atoms being along the trigonal axes. The order of magnitudes of the frequencies will therefore be the same as that shown in Table IV. But, here again, the consideration of T which is negative, may possibly reverse the order so far as modes I and II are concerned. The spectrum consists of two high frequencies, one medium and one very low frequency.

In conclusion the author's grateful thanks are due to Prof. Sir C. V. Raman for his kind interest in the work.

Summary

Exact expressions have been derived for the frequencies of the eigenvibrations of the face-centred and body-centred cubic lattices in terms of 6 and 5 force constants respectively, the constants in each case being connected by one additional relation.

INFLUENCE OF TEMPERATURE ON THE RAMAN SPECTRA OF CRYSTALS

Part I. Calcite

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1. Introduction

The subject dealt in the series of papers of which this is the first has interested investigators ever since the beginnings of Raman spectroscopy, and quite an extensive literature has grown up around the topic. It has been noticed by several investigators that whereas, at least in the majority of cases, the frequency shifts recorded with crystals at room temperature appear as very sharp lines, this feature becomes much less marked when the crystal is heated up. *Per contra*, in those few cases where the lines are a little diffuse at ordinary temperatures, they sharpen remarkably when the crystal is cooled down to low temperatures. Other effects have also been noticed, *viz.*, a diminution of the frequency shifts with rising temperature, as also a notable falling off in the intensity of the lines. With regard to the latter, one must distinguish between a diminution of the peak intensity which is naturally to be expected when a line broadens, and a falling off in the integrated intensity of the line. According to Placzek's theory of the Raman effect, the intensity of the Raman lines of a crystal should increase sensibly when it is heated up. That the contrary is the case has been reported by several investigators. It must be emphasized that all the effects observed vary notably from line to line in the Raman spectrum of a crystal, even in respect of order of magnitude.

From a theoretical point of view, the subject is of prime importance in view of its bearing on the fundamental problem of the nature of the vibration spectrum of a crystal, as also of its relation to the various thermodynamic properties of a crystal, *viz.*, its specific heat, the thermal expansion, the thermal conductivity, the influence of temperature on the elastic properties of the crystal and so forth. Any theory which claims to explain these various properties must in the first instance be capable of giving a satisfactory account of the spectroscopic behaviour of crystals and of the manner in

which it is influenced by temperature. In other words, the data furnished by Raman spectroscopy with crystals form the touchstone for testing theories of the solid state. Hence arises the importance of a precise and extended knowledge of experimental facts.

A survey of the literature indicates the need for a thorough revision of the whole field. The data obtained by different investigators with the same crystal often differ notably. Owing evidently to the difficulties of experimentation, data have mostly been reported for a few of the more intense lines in the spectrum and not for all. The observations made usually also refer only to a few isolated temperatures instead of to a sufficient number spread out at intervals over the widest possible range. Further, it is not unusual to find that some aspects of the subject have been considered and not others, whereas the need for a correlated study of all of them is obvious. These deficiencies in the literature have induced the author to undertake a systematic exploration of the subject. The crystals taken up for study have been so chosen that the well-known Rasetti technique utilizing the intense λ 2536 radiation of a water-cooled magnet-controlled mercury arc in quartz can be applied. This technique enables spectrograms showing even the faintest lines to be obtained with reasonable exposures, and also enables the higher dispersion and resolution provided by quartz spectrographs in the ultra-violet to be availed of to obtain greater precision in the measurements. It may be remarked that all the earlier investigators in the field have used the λ 4358 excitation which is much less satisfactory from every point of view.

2. Previous Work on Calcite

The temperature variations in the Raman frequencies of calcite were first studied by Ornstein and Went (1935) who recorded the spectrum at 90°, 293°, 367° and 426° K, and came to the following conclusions. As the temperature is raised, the Raman lines show a decrease in frequency shift. This decrease is greater for the low frequency lattice lines than for the high frequency lines. In fact they could detect no such decrease in the latter. Regarding the width of the Raman lines, the authors found the width to be proportional to the square root of the absolute temperature and to increase greatly with temperature. Kopcewicz (1937) conducted experiments at 293° K and at 683° K and noticed that the lattice lines with frequency shifts 155 cm.$^{-1}$ and 281 cm.$^{-1}$ show a marked shift towards the exciting line. He could detect shifts of 5 and 4 cm.$^{-1}$ in the position of the internal frequencies at 711 and 1433 cm.$^{-1}$ respectively, but found no change in the symmetrical frequency at 1085 cm.$^{-1}$ Venkateswarlu (1942) in the course of his study of the variations in intensity of the Raman lines, observed considerable shifts

in the position of the lattice lines with increase of temperature but noticed no change in the positions of the other lines.

3. Experimental Details

Low temperatures.—For the study of the Raman Spectra below the room temperature, a demountable vacuum flask with an inner vessel of brass and a glass outer vessel was used. Two quartz windows were fixed at the bottom end of the glass vessel. Through one of these, the crystal of calcite was irradiated with light from the mercury arc while through the other the scattered light was led to the slit of the spectrograph. The specimen used for low temperature work was a thin piece of calcite which was fixed on a copper block attached to the bottom of the inner brass vessel which formed the container for the refrigerant. The flanged joint between the inner brass tube and the outer glass vessel was sealed with Apiezon sealing compound "Q" and the flask was kept continuously evacuated by a Cenco Hyvac pump.

High temperatures.—For work above room temperature, a heater capable of withstanding high temperatures was constructed. It consisted of a rectangular metallic box ($1\frac{1}{2}'' \times 1'' \times \frac{1}{2}''$) with the two ends open. A window ($\frac{1}{2}'' \times \frac{1}{4}''$) was cut open on one of the broader sides of the box for irradiation purposes and was closed by a fused quartz disc stuck over it. The box was surrounded by a thin layer of mica over which was closely wound nichrome wire and set in a mixture of sodium silicate solution and alumina powder. The entire heater was then plastered with a paste of asbestos. The specimen of calcite used for high temperature work was a piece cleaved along natural faces ($\frac{3}{4}'' \times \frac{1}{2}'' \times \frac{1}{4}''$). It was kept inside the heater without coming into contact with the metallic portions by mica strips suitably stuffed in the vacant spaces, leaving enough air space inside. One broad side of the crystal was kept facing the window for irradiation and the scattered light was taken from one of the edges. The open ends of the heater were then closed with mica strips, one of which contained a rectangular opening through which the scattered light from the crystal could be led out. Thus the air inside the heater also attained the temperature of the furnace.

The heating current was supplied from a set of accumulators, except for very high temperatures when direct current from the mains was drawn through a series of resistances. To determine the temperature of the calcite piece during an experiment, a calibrated nichrome-constantan thermocouple was fixed inside the furnace touching the crystal. The temperature of the crystal during an exposure was always kept constant by regulating the current passed. At the highest temperature reached, *viz.*, 700° K, the furnace took about 30 minutes to attain a steady state.

For the study of the variations of the position and width of the intense Raman lines, a Hilger E3 medium quartz spectrograph with a dispersion of about 140 cm.$^{-1}$/mm. in the λ 2536 Å region was used. With a slit width of ·04 mm., exposures of the order of 3 hours each were given to obtain reasonably intense spectrograms. In order to measure the position of the lines accurately, a comparison iron arc spectrum was always partially superposed over the Raman spectrum at each temperature. Ilford Special Rapid plates were usually used and the negatives were measured under a Hilger Cross slide micrometer, reading up to 1/1000 mm.

In order to measure the total shift in the two other fainter lines in calcite *viz.*, 710 and 1433 and to demonstrate clearly the shift and broadening in all the Raman lines of calcite, two photographs, one at room temperature and the other at the highest temperature possible, *viz.*, 710° K of the Raman spectrum of calcite, were recorded in juxtaposition on the same plate with the help of a Hartmann diaphragm using the large E1 spectograph having a dispersion of about 44 cm.$^{-1}$/mm. in the λ 2536 Å region. With a slit width of ·06 mm., exposures of the order of 12 hours at room temperature and 24 hours at high temperature were given. This plate was microphotometered under a Moll's microphotometer.

With the smaller instrument, the frequency and width changes of the strong Raman lines were determined at seven different temperatures above 300° K, *viz.*, 343°, 398°, 438°, 508°, 583°, 638° and 698° K. Using liquid air and solid carbon dioxide—alcohol mixture, two low temperature pictures at 90° K and 185° K, were also obtained.

4. Results

The variations observed in the position and width of the two lattice lines of calcite at 155 and 281 cm.$^{-1}$ and in the internal symmetric frequency at 1085 cm.$^{-1}$ measured directly, are put down in Table I. The total change in frequency shift in all the Raman lines from room temperature to the highest and the proportional change $1/\nu \cdot d\nu/dT$ are given in Table II. Five typical spectrograms taken with an E3 instrument showing the gradual decrease in the frequency shifts and increase in breadth of the Raman lines with rising temperature are reproduced in Fig. 1 (Plate XXIV). Contrary to the conclusions reached by previous authors, the symmetric oscillation with frequency shift 1085 cm.$^{-1}$ does show a clear temperature variation in its position. This and the changes in the position and width in the other fainter internal frequencies, as also the tremendous influence of temperature on the lattice lines are clearly seen from the E1 spectrogram reproduced in Fig. 2 (Plate XXIV) and its microphotometric record reproduced in Fig. 3.

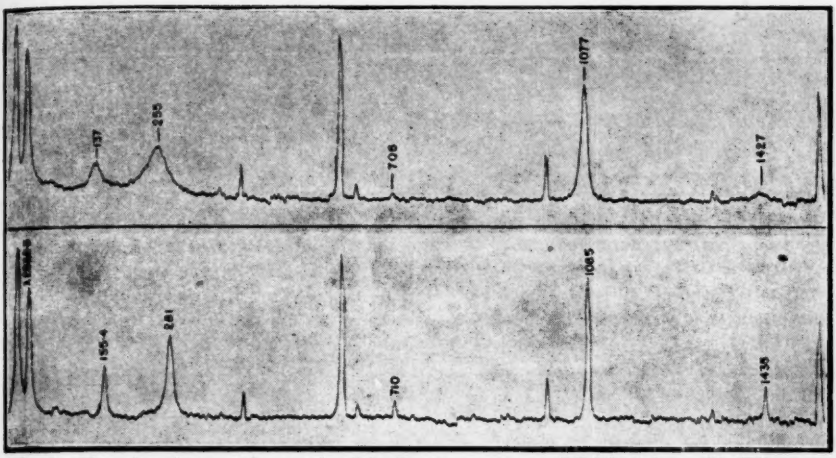

Fig. 3. The microphotometric records of the Raman spectrum of Calcite taken with (E1) spectrograph showing the shift, broadening and decrease in peak intensity of the Raman lines at high temperature.

The temperature variations of the intense 155, 281 and 1085 lines are graphically represented in Figs. 4, 5 and 6 respectively.

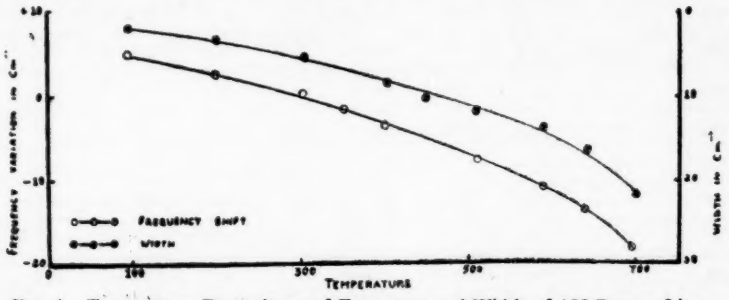

Fig 4. Temperature Dependence of Frequency and Width of 155 Raman Line

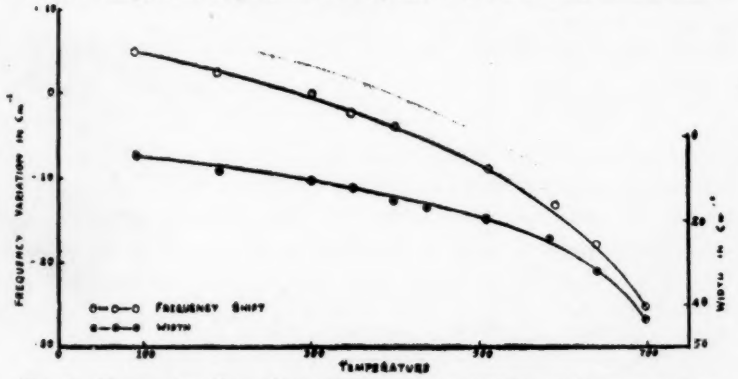

Fig. 5. Temperature Dependence of Frequency and Width of 281 Raman Line

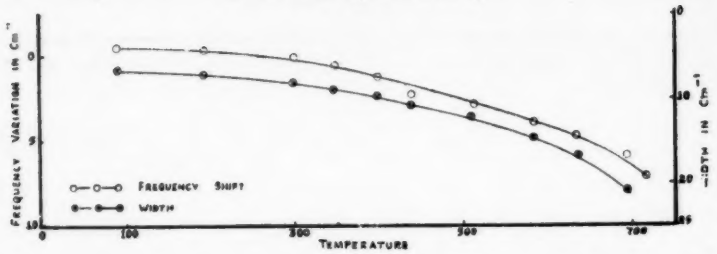

FIG. 6. Temperature Dependence of Frequency and Width of 1085 Raman Line

TABLE I

Temperature variation of the position and width of the prominent Raman lines in Calcite

Temperature K°	ν=155 cm.$^{-1}$			ν=281 cm.$^{-1}$			ν=1085 cm.$^{-1}$		
	Centre of line cm.$^{-1}$	Shift cm.$^{-1}$	Breadth cm.$^{-1}$	Centre of line cm.$^{-1}$	Shift cm.$^{-1}$	Breadth cm.$^{-1}$	Centre of line cm.$^{-1}$	Shift cm.$^{-1}$	Breadth cm.$^{-1}$
90	161·1	4·7	3	286·1	5·1	5	1085·0	0	5·6
185	157·2	1·9	4	283·0	2·0	9	1085·0	0	7·0
300	155·4	0	6·1	281·0	0	10	1085·0	0	8
343	153·2	2·2	9·1	278·2	2·9	12·6	1084·3	0·7	8·5
398	150·2	4·2	9·9	275·3	4·3	15·9	1083·5	1·5	9·1
438	148·9	6·5	10·6	272·8	7·2	16·8	1082·7	2·3	10·6
508	147·7	7·7	11·7	271·8	9·2	20	1082·0	3·0	11·8
583	144·6	10·8	13·5	267·9	13·1	24·1	1081·4	3·6	13·5
638	141·6	13·8	16·0	263·1	17·9	31·8	1080·4	4·6	16·9
698	137·5	17·9	22·0	256·0	25·0	44·0	1079·5	5·5	21·8

TABLE II

Total shift and proportional change in the position of Raman lines in Calcite

Raman line cm.$^{-1}$	$\nu_{300°}$ cm.$^{-1}$	$\nu_{700°}$ cm.$^{-1}$	$d\nu$ cm.$^{-1}$	$\chi = 1/\nu \cdot d\nu/dT$
155	155·4	137·5	17·9	289×10^{-6}
281	281·0	256·0	25·0	225×10^{-6}
710	710·0	706·0	4·0	14×10^{-6}
1085	1085·0	1079·5	5·5	13×10^{-6}
1435	1435·0	1427·0	8·0	14×10^{-6}

From room temperature to that of liquid air the lattice lines show a definite increase in the frequency shift. The line 155 cm.$^{-1}$ for which Ornstein and Went could not notice any change in position, exhibits a variation by about 4·7 cm.$^{-1}$ Because the specimen used for low temperature work was necessarily a thin piece, the spectrograms obtained could not be reproduced properly although they could be measured. The variation in frequency shift recorded by Kopcewicz for the two lattice lines 155 and 281 cm.$^{-1}$ for the temperature range 293° to 700° K was 10 and 11 cm.$^{-1}$ respectively whereas for the same range, the present author has measured a change corresponding to 17·5 and 25 cm.$^{-1}$ respectively for the same lines. The internal frequency at 710 cm.$^{-1}$ shows a variation of about 4 cm.$^{-1}$ and the one at 1435 cm.$^{-1}$ shifts by about 8 cm.$^{-1}$

5. Discussion

Temperature and frequency shift.—The results obtained from the present study show conclusively that all the Raman lines of calcite exhibit measurable variations in frequency shift. The two lattice lines, on cooling down to liquid air temperature show an appreciable increase in frequency shift while the other three lines are apparently unaffected. At high temperatures, the lattice lines shift towards the exciting line to a far greater extent than the other three lines. The proportional change $d\nu/\nu$ in frequency shift is about 0·1 for the low frequency lines, whereas for the internal oscillations it is about 0·005.

The two lattice lines arise, as is well known, from (i) a longitudinal motion of the CO_3 groups in a direction transverse to the trigonal axis and (ii) a rotatory oscillation of these groups around an axis in their plane. The magnitude of these oscillations is determined by the interionic forces which will be greatly affected by variations of temperature, and hence the lattice lines exhibit considerable temperature effect. On the other hand, the lines due to the internal oscillations of the CO_3 group are not influenced to the same extent by temperature variations, indicating that the inter-atomic forces inside the CO_3 ion are less temperature sensitive than the lattice forces. Similar results have been reported by Nedungadi (1939) for $NaNO_3$ which has the same structure as $CaCO_3$.

In studies of the temperature variation of the various properties of crystals, the vibrational frequency is usually encountered in the form of the expression $1/\nu.\ d\nu/dT$ denoted by χ. The mean χ values for the various frequencies for the temperature range 300° to 700° K are entered in Table II. For the 155 cm.$^{-1}$ line, χ for the temperature range 85° to 300° K is 141×10^{-6} and for the range 583° to 698° K, it is $387{\cdot}1 \times 10^{-6}$. For the same ranges

of temperature, it is $84{\cdot}4 \times 10^{-6}$ and $368{\cdot}2 \times 10^{-6}$ for the 281 cm.$^{-1}$ line. The χ value for the 1085 oscillation is 0 for the range 85° to 300° K and 24·3 for the range 583° to 698° K. It will thus be seen that χ is not constant but goes on increasing with temperature for all the frequencies. It is significant that while for the lattice lines it tends to become zero at low temperatures but does not actually attain that value, χ for the internal symmetrical oscillation at 1085 cm.$^{-1}$ is actually zero at low temperatures. This is clear from Figs. 4, 5 and 6, which graphically represent the influence of temperature on the Raman lines. Whereas for the 1085 line, the curve is almost flat at very low temperatures, it is not exactly flat though it tends to become so, for the lattice frequencies over the corresponding range of temperature. The mean χ value obtained for the 1085 line is $13{\cdot}0 \times 10^{-6}$ which compares very well with the value 15×10^{-6} obtained for the corresponding symmetrical oscillation at 1065 cm.$^{-1}$ for $NaNO_3$, by Nedungadi (1939). There is also good agreement with the χ values for the electronic frequencies λ 1000 Å and λ 1535 Å in ultra-violet absorption calculated by Ramachandran (1947) from his equations for the thermal variations of the refractive indices of calcite, based on the data of Reed (1898). Table III gives the χ values for λ 1000 Å calculated by Ramachandran and those obtained by the present author for the 1085 cm.$^{-1}$ Raman line.

TABLE III

Temperature °C.	$\chi \times 10^6$ for λ 1000	$\chi \times 10^6$ for 1085 cm.$^{-1}$
61·5	10·6	13·5
152·1	14·6	17·1
349	24·0	24·6

Temperature and width of Raman lines.—As pointed out earlier, the time of exposure for obtaining the Raman spectra was reduced to the minimum by the use of the λ 2536 radiation as the exciter, and therefore the measurements of width of the Raman lines in Table I can be said to be free from errors due to photographic factors. The temperature of the furnace was also kept constantly regulated and never allowed to fluctuate by more than $\pm$ 2°. It will be evident from Fig. 1 that at low temperature, the Raman lines are fairly sharp and well defined. As the temperature is increased, they become broader and spread over a finite range of values. This is true of both the lattice and internal frequencies. At high temperatures, there is asymmetry in the broadening of the lines as will be evident from the

microphotometric record reproduced in Fig. 3, and this is more so in the case of the lattice lines. In general, the increase in width with temperature is of the same order of magnitude as the decrease in frequency shift, the former being always greater than the latter. Similar broadening of the Raman lines has been reported by Nedungadi for $NaNO_3$.

It will be seen from Figs. 4, 5 and 6 that the temperature-frequency shift and the temperature-width curves for the Raman lines in calcite are strikingly similar in shape. At low temperatures, the curves tend to become horizontal and the rate of change is greater at higher temperatures. This similarity, together with the fact that their magnitudes are also of the same order, suggests that the variations of frequency shift and width of the Raman lines with temperature are closely related to each other. This lends support to the idea that the variations caused in the Raman spectra by temperature can be successfully explained by taking into account the role played by mechanical and electrical anharmonicities in relation to the thermally excited energy levels of the crystals, as has been indicated by Sir C. V. Raman (1947).

Measurements of the total intensities of the Raman lines which involve exacting conditions of experiment have not yet been completed. It will be evident, however, from Fig. 3 that there is a definite reduction in peak intensity of the Raman lines with increase of temperature.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his valuable guidance and keen interest in this investigation.

Summary

With the λ 2536 radiation of the mercury arc as exciter, the Raman spectrum of calcite has been studied at the temperatures 90°, 185°, 300°, 343°, 398°, 438°, 508°, 583°, 638° and 698° K. It is found that *all* the Raman lines exhibit definite decrease in frequency shifts with increase in temperature, the decrease being much greater in the case of the lattice lines than in the internal oscillations of the CO_3 group. The width of the Raman lines increases with temperature and this increase is of the same order of magnitude in each case as the diminution of frequency shift, the former being always greater than the latter. The temperature-frequency shift, and the temperature-width curves for the various Raman lines exhibit a striking similarity in shape, tending to flatten up at low temperatures and the rate of change being greater at high temperature, suggesting a close relationship between the two. The peak intensity of the Raman lines is also found to decrease very much with rising temperature.

References

1. Ornstein and Went .. *Physica*, 1935, **2**, 503.
2. Went, J. J. .. *Doctorate thesis*, University of Utrecht, 1935.
3. Kopcewicz, C. .. *Journ. de Phys. et Radium* 1937, **8**, 6.
4. Venkateswarlu .. *Proc. Ind. Acad. Sci.* A, 1942, **16**, 45.
5. Nedungadi, T. M. K. .. *Ibid.*, 1939, **8**, 397.
6. Ramachandran, G. N. .. *Ibid.*, 1947, **26**, 87.
7. Raman, C. V. .. *Ibid.*, 1947, **26**, 339.
8. Reed .. *Ann. d. Phys. u. Chem.*, 1898, **65**, 734.

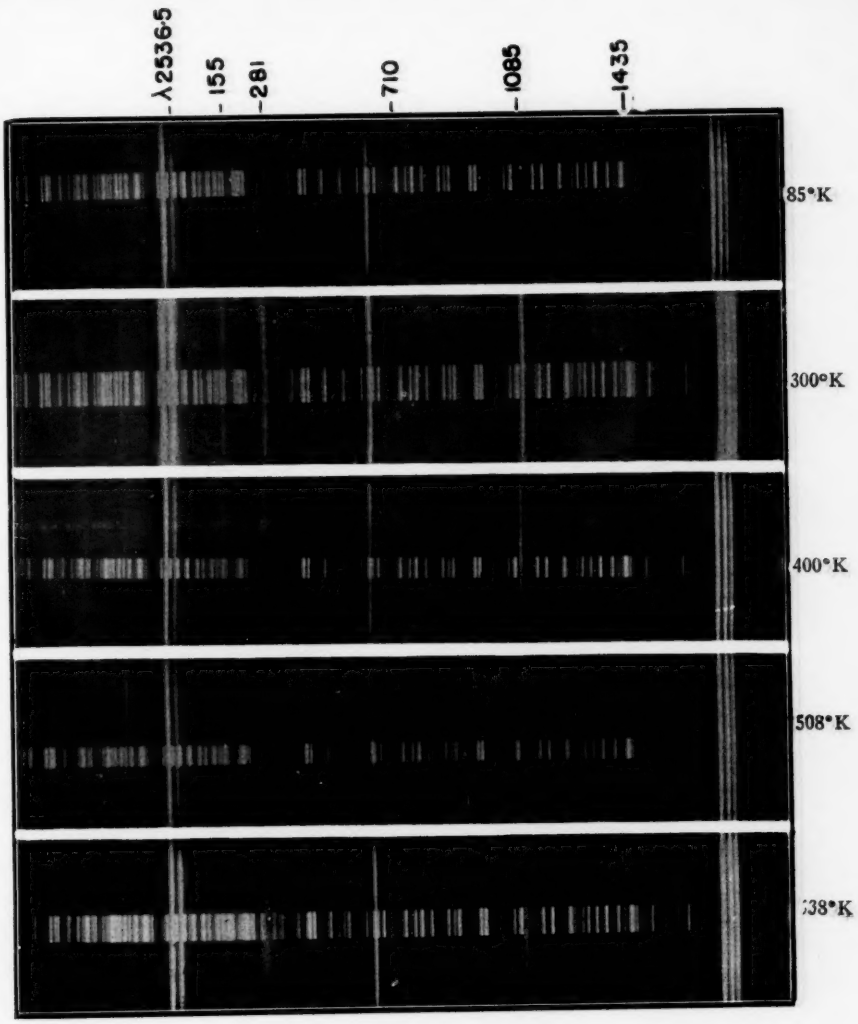

FIG. 1. Raman Spectrum of Calcite taken with E3 spectrograph

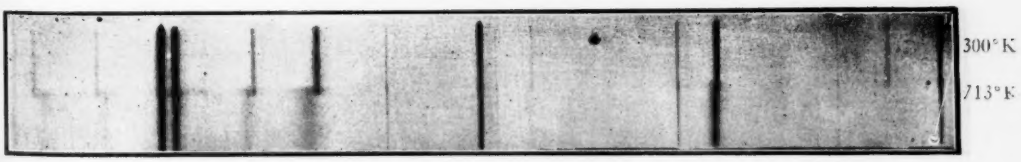

FIG. 2. Raman Spectrum of Calcite taken with E1 spectrograph using Hartmann diaphragm

INFLUENCE OF TEMPERATURE ON THE RAMAN SPECTRA OF CRYSTALS

Part. II. Quartz

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1. Review of the Previous Work on Quartz

The effect of temperature on the Raman Spectrum of quartz has been studied by several workers, mostly in connection with the variations in intensity of the Raman lines. Landsberg and Leontowitsch (1929) and Landsberg and Mandelstam (1929, 1930) were among the earliest who studied the variations in the intensity of the Stokes and anti-Stokes Raman shifts, especially the one at 466 cm.$^{-1}$ within the temperatures 18° to 500° C. Brickwedde and Peters (1929) investigated the Raman spectrum of quartz at temperatures − 180° to 550° C. over the range 2000 to 5000 Å. They observed that the intensity of the anti-Stokes line at 466 cm.$^{-1}$ rises with temperature and that the displacements from the exciting line corresponding to the 466 and 128 cm.$^{-1}$ Raman lines decrease with increase of temperature. The line at 466 cm.$^{-1}$ which was sharp at room temperature was found to become diffuse at high temperature. Ney (1931) reported, from a study of the Raman spectrum over the range 18° to 500° C. that there is a marked diminution in the frequency shifts of the prominent Raman lines in quartz. He observed that the lines at 125, 203 and 463 cm.$^{-1}$ shift to 99, 175 and 457 cm.$^{-1}$ respectively at the highest temperature. Ornstein and Went (1935) measured the variations in the intensity and position of the 127 and 465 Raman lines at 90, 294, 360 and 420° K. They noticed that the breadth of the Raman lines increased with temperature and found it to be proportional to the square root of absolute temperature. Disagreement with theory regarding the intensity of the Raman lines at higher temperatures was reported by them, as also by Venkateswarlu (1941). So far, the most complete results are those given by Nedungadi (1940) who studied the changes in frequency shift and the breadth of the more prominent Raman lines in quartz, *viz.*, 127, 207 and 466 lines at − 180, 25, 100, 200, 300, 410 and 530° C. He also measured the total variation in the position of many of the other lines from the lowest

to the highest temperature. The extraordinary behaviour of the 207 cm.$^{-1}$ line which broadens out enormously and ultimately disappears as the temperature is raised, was pointed out by him. Raman and Nedungadi (1940) suggested that this behaviour of the 207 cm.$^{-1}$ line with rising temperature has a special importance in the α–β transformation of quartz which occurs at the transition temperature 575° C.

2. Details of the Experiment

The specimen of quartz used for these investigations was a transparent piece ($\frac{3}{4}'' \times \frac{1}{2}'' \times \frac{1}{4}''$). The heater used and the optical arrangements for obtaining the Raman spectra at different temperatures were the same as described in Part I of this series. The spectra were excited by λ 2536 resonance radiations of a quartz mercury arc. As in the experiments with calcite, two quartz spectrographs, Hilger E1 and E3 were employed. The medium instrument was used to study the variations in position and width of the prominent Raman lines in quartz with the temperature at 85, 300, 338, 378, 438, 493, 543, 593 and 685° K. With a slit width of 0·04 mm., exposures of the order of 2 hours each were necessary to obtain reasonably intense spectrograms. With the large E1 instrument, two pictures, one with the crystal at room temperature and the other with the crystal at the highest temperature possible were taken in juxtaposition using a Hartmann diaphragm, in order to show the effect of temperature on the various Raman lines in a clear way.

3. Results

Five typical spectrograms taken with the E3 instrument showing the variations in the frequency shift and width of the Raman lines in quartz with rising temperature are reproduced in Fig. 1 (Plate XXV). The picture taken with the large E1 instrument using a Hartmann diaphragm is reproduced in Fig. 2 (Plate XXVI).

The measured variations in position and breadth of the three prominent Raman lines at 128, 207 and 466 cm.$^{-1}$ are given in Table I. The changes observed in the position of three of the less prominent lines at 265, 357 and 695 cm.$^{-1}$ are contained in Table II. The variations in the width of these lines were not large enough to need detailed tabulation. The total changes in frequency shift and width for all the important Raman lines in quartz along with the proportional change χ are given in Table III.

The microphotometric record of the E1 spectrogram is reproduced in Fig. 3. This shows vividly the influence of temperature on the Raman lines in quartz with regard to their position and width. The temperature

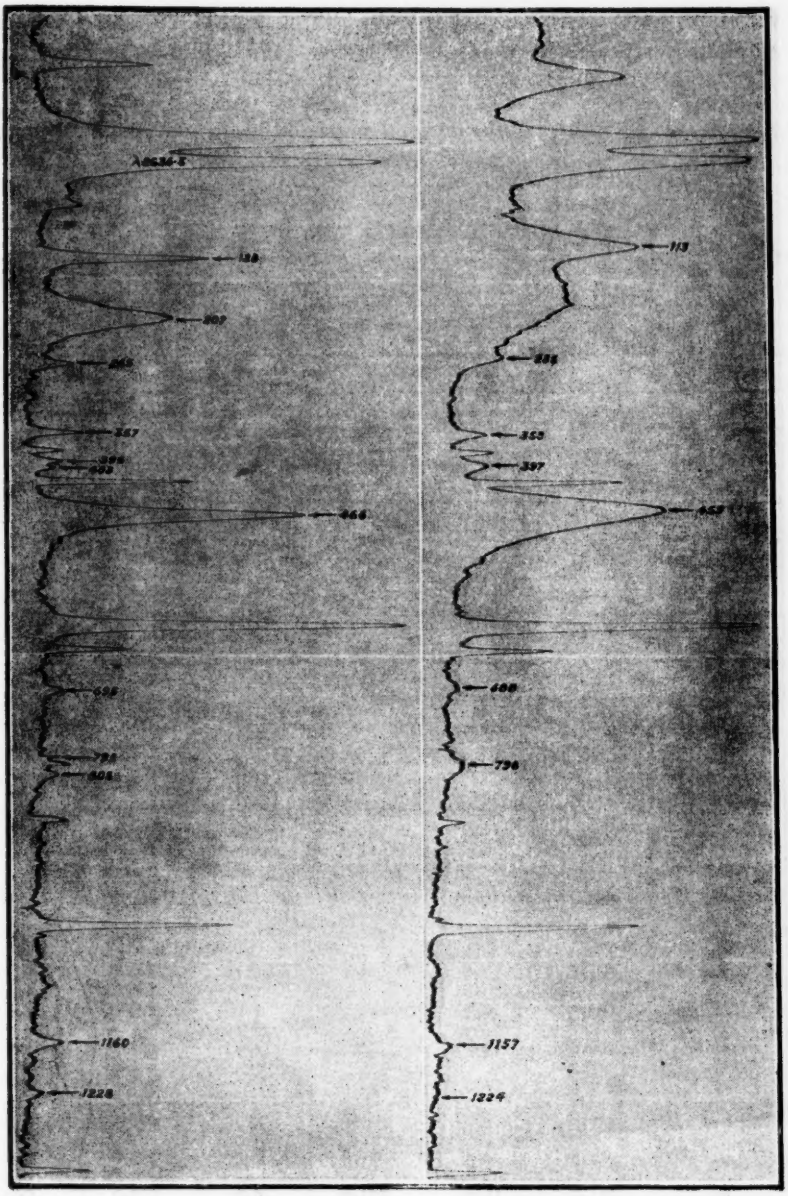

FIG. 3. Microphotometric record of the Raman Spectrum of quartz taken with E1 spectrograph showing change in position and broadening of the different Raman lines

variations in the frequency shift and width of the 128, 207 and 466 lines are graphically represented in Figs. 4, 5 and 6. Fig. 7 shows the variation in

TABLE I

Temperature variations in the position and width of the prominent Raman lines in quartz

Temperature °K	ν = 128 cm.$^{-1}$			ν = 207 cm.$^{-1}$			ν = 466 cm.$^{-1}$		
	Position cm.$^{-1}$	Shift cm.$^{-1}$	Width cm.$^{-1}$	Position cm.$^{-1}$	Shift cm.$^{-1}$	Width cm.$^{-1}$	Position cm.$^{-1}$	Shift cm.$^{-1}$	Width cm.$^{-1}$
85	131·5	3·5	4·0	218·5	11·5	8·0	468·0	2·0	6·0
300	128·0	0	8·5	207	0	18	466	0	12
338	126·5	1·5	9·0	205·5	1·5	20·5	465·6	0·4	13
378	124·7	3·3	10·0	203·5	3·5	23·0	465·2	0·8	14·5
438	122·4	5·6	11·5	201·1	6·9	28·0	465·0	1·0	16·5
493	120·0	8·0	13·5	196·0	11·0	36·0	464·1	1·9	19·0
543	116·8	11·2	16·0	189·8	17·2	46·0	462·5	3·5	22·5
593	112·7	15·3	21·0	182·7	24·3	58·0	460·2	5·8	27·0
685	106·1	21·9	28·0	172·6	34·4	75·0	457·0	9·0	35·0

TABLE II

Variations in frequency shift observed in some of the other Raman lines

Temperature °K	ν = 265 cm.$^{-1}$		ν = 357 cm.$^{-1}$		ν = 695 cm.$^{-1}$	
	Position cm.$^{-1}$	Shift cm.$^{-1}$	Position cm.$^{-1}$	Shift cm.$^{-1}$	Position cm.$^{-1}$	Shift cm.$^{-1}$
85	267·2	2·2	358·0	1·0	696·0	1·0
300	265·0	0	357·0	0	695·0	0
338	264·0	1·0	357·0	0	695·0	0
378	262·5	2·5	356·0	1·0	694·6	0·4
438	262·5	2·5	355·5	1·5	694·0	1·0
493	261·5	3·5	354·5	2·5	693·0	2·0
543	259·5	5·5	354·0	3·0	691·8	3·2
593	257·0	8·0	352·8	4·2	689·0	6·0
685	254·0	11·0	351·0	6·0	686·0	9·0

TABLE III

Total change in frequency shift and width of the important Raman lines in Quartz and the proportional change χ

Raman line centre at 300°K $\nu_{300°}$ in cm.$^{-1}$	Centre of the line at 685·K $\nu_{685°}$ in cm.$^{-1}$	Shift $d\nu$ in cm.$^{-1}$	Proportional change $\chi=(1/\nu)\,d\nu/dT$	Breadth at 300°K in cm.$^{-1}$	Breadth at 685°K in cm.$^{-1}$
128·0	106·1	21·9	450×10^{-6}	8·5	28·0
207·0	172·6	34·4	430×10^{-6}	18·0	75·0
265·0	253·5	11·5	112×10^{-6}	3·5	8·5
357·0	351·0	6·0	43×10^{-6}	3·0	10·0
395·0	397·0			3·5	15·0
403·0				3·5	
466·0	457·0	9·0	50×10^{-6}	12·0	35·0
695·0	686·0	9·0	35×10^{-6}	6·0	12·0
795·0	796·0			4·0	18·0
805·0				4·0	
1160·0	1156·0	4·0	$8·9\times10^{-6}$	5·0	11·0
1228·0	1223·0	5·0	$9·8\times10^{-6}$	5·5	13·0

frequency shift of the 357 and 265 Raman lines with temperature. The changes in the 695 and other lines, being of the same order are not plotted separately.

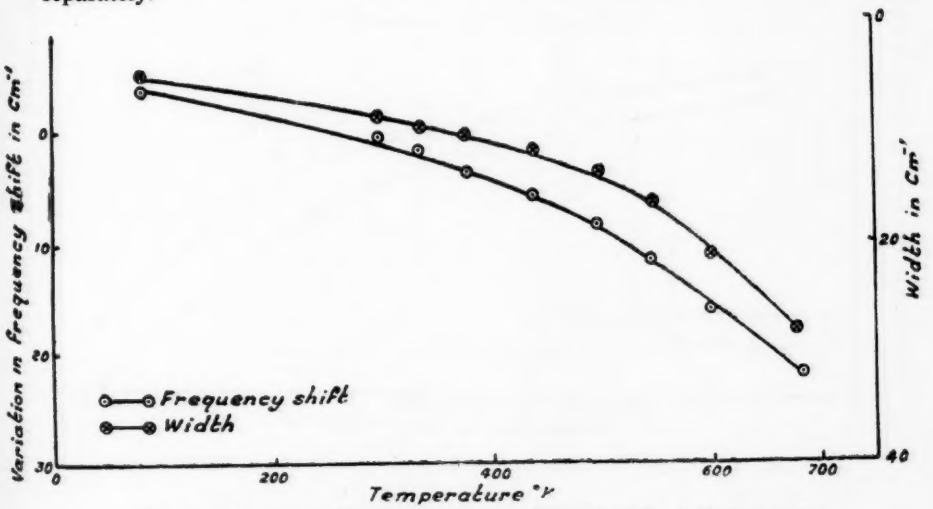

FIG. 4. Temperature Dependence of the position and width of 128 Raman line

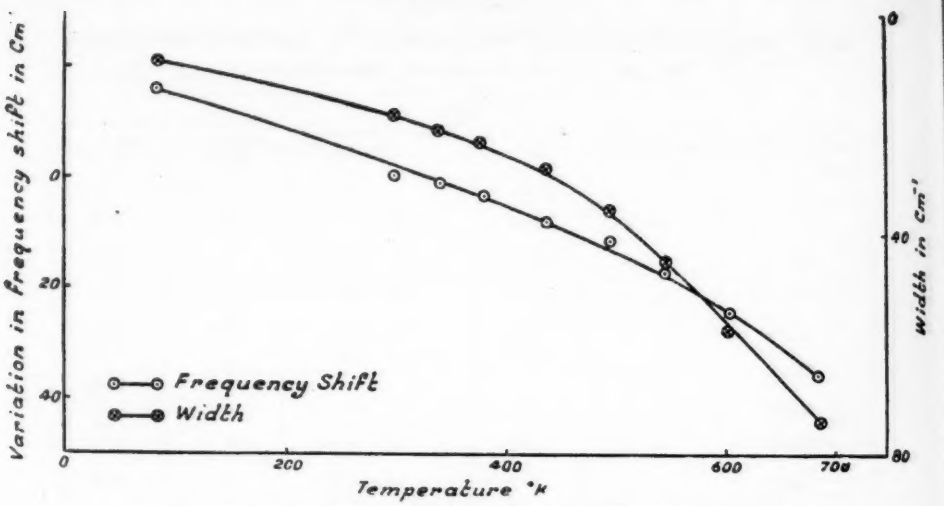

FIG. 5. Temperature Dependence of the position and width of 207 Raman line

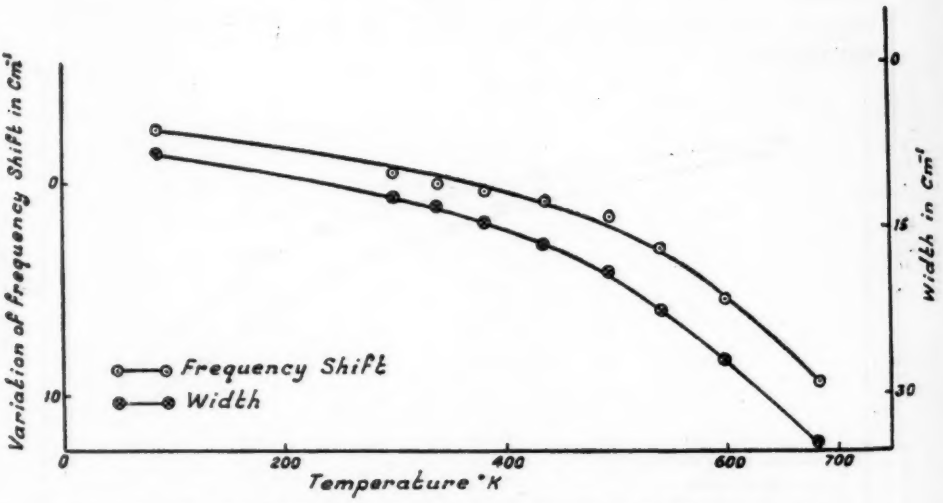

FIG. 6. Temperature Dependence of the position and width of 466 Raman line

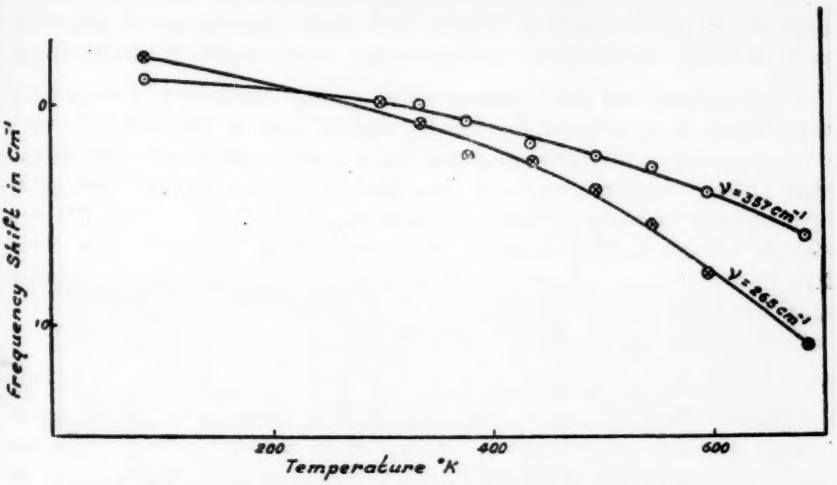

FIG. 7. Temperature Dependence of the position of the 265 and 357 Raman lines

It will be evident from the tables that all the Raman lines exhibit measurable shifts in their position at high temperatures. This shift is much greater in the case of the Raman lines 128, 207, 265 and 466, than in the other lines. The greatest diminution is found in the 207 cm.$^{-1}$ line which shifts by about 46 cm.$^{-1}$ from 85° to 685° K. At higher temperatures the line broadens out considerably and the measured shifts are only approximate. This line sharpens appreciably on cooling from room temperature to that of liquid air as will be seen from Fig. 8. An interesting feature observed on

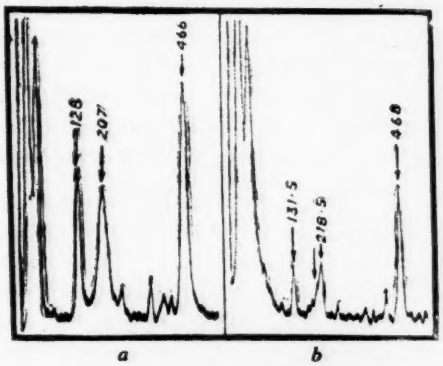

FIG. 8. Raman Spectrum of Quartz
(*a*) at room temperature (*b*) at liquid air temperature

cooling is the apparent splitting up of this line into at least one more component, shown by an arrow in Fig. 8. A careful examination of this point is to be made shortly by the author using a larger dispersion spectrograph.

The 128 and 466 cm.$^{-1}$ Raman shifts are also observed to broaden out considerably with temperature, but the Raman lines at 265 and 357 cm.$^{-1}$, do not broaden out to the same extent and remain comparatively well defined even at high temperatures. The two lines at 395 and 403 cm.$^{-1}$ merge at high temperatures into a band extending by about 15 cm.$^{-1}$ The 795 and 805 cm.$^{-1}$ lines similarly form a band about 18 cm.$^{-1}$ broad. The other Raman lines beyond 600 cm.$^{-1}$ also are found to broaden appreciably with temperature.

4. Discussion

Temperature and frequency shift.—The variation in frequency shift for the different Raman lines is not uniform with temperature. This is evident from a consideration of χ, the proportional change for the different ranges of temperature for each Raman line. χ for the 128 cm.$^{-1}$ line is 127×10^{-6} for the temperature range 85 to 300° K. and 590×10^{-6} for the range 543 to 685° K. For the 207 cm.$^{-1}$ line, the χ value is 255×10^{-6} and 585×10^{-6} respectively for the same ranges of temperature. In the case of the 466 cm.$^{-1}$ line, the value at low temperature range is 20×10^{-6} and for the high temperature range it is 80×10^{-6}. The χ value is seen to rise with increasing temperature. At low temperatures, it tends to become zero but does not actually attain it. For the 207 cm.$^{-1}$ line which exhibits remarkable temperature variations, the value of χ is high even at the low temperature range, being as much as 255×10^{-6}. This is clearly seen from the temperature-frequency shift curves drawn in Figs. 4, 5 and 6. In Fig. 5, the curve for the 207 cm.$^{-1}$ line is found to have a considerable slope even at low temperatures, whereas in Figs. 4 and 6, the curves for 128 and 466 cm.$^{-1}$ lines are found to be almost flat at the corresponding range. The temperature-frequency shift curves for all the Raman lines are of a similar nature. The rate of decrease *i.e.*, $-\mathrm{d}\nu/d\mathrm{T}$ is greater at high temperatures.

The mean χ values for the different Raman lines for the temperature range 300–685° K. are given in Table III. The χ ranges from 450×10^{-6} in the case of the 128 cm.$^{-1}$ line to $8{\cdot}9 \times 10^{-6}$ in the case of the 1228 cm.$^{-1}$ line. The general finding that the low frequency oscillations give maximum χ values and that the high frequency ones give the minimum values is observed to hold good in the case of quartz also. Thus we find that the lowest frequency shift 128 cm.$^{-1}$ has the highest χ value of 450×10^{-6}, the 207 cm.$^{-1}$ line has the next highest and so on and the highest frequency shift

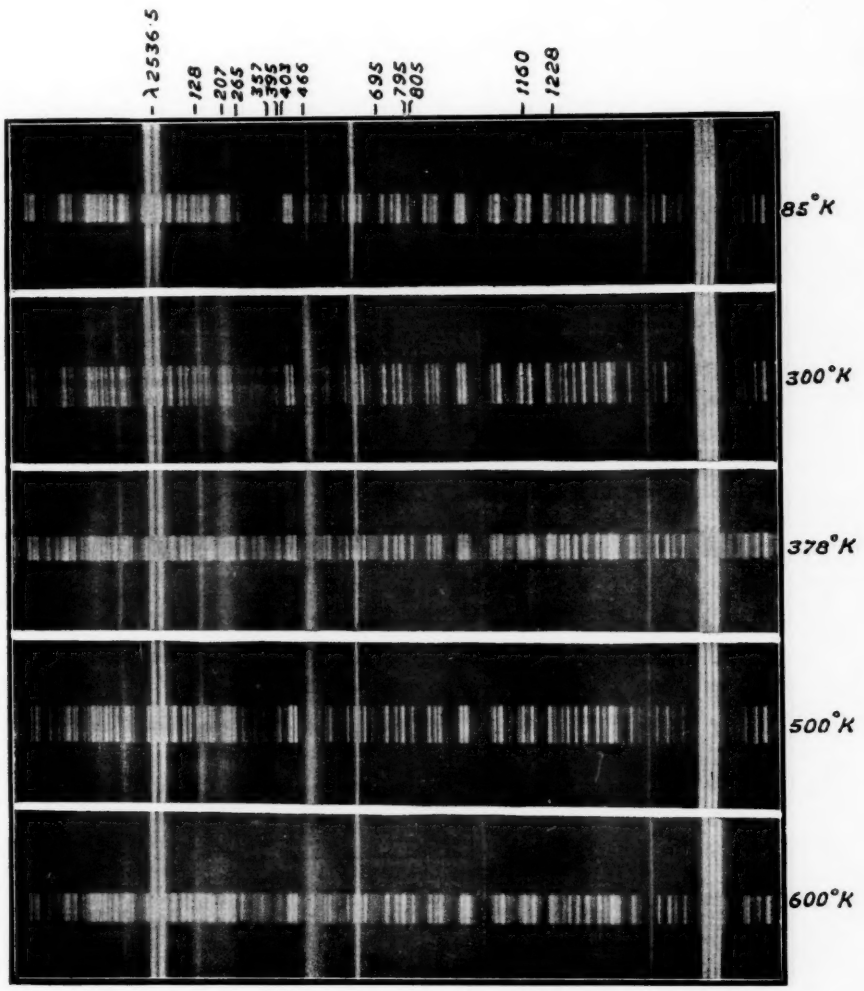

FIG. 1. Raman spectra of quartz taken with E 3 spectrograph

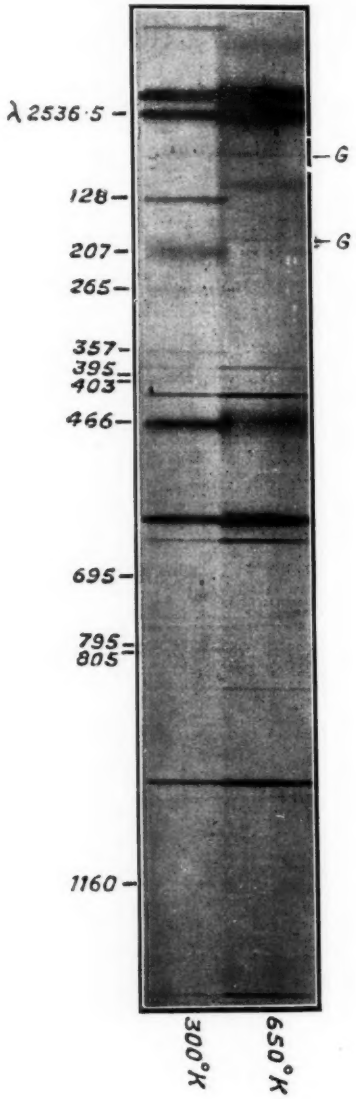

FIG. 2. Raman spectrum of quartz taken with E1 spectrograph using Hartmann diaphragm

1228 cm.$^{-1}$ has the lowest χ value of $8{\cdot}9 \times 10^{-6}$. Broadly speaking, we may divide the Raman lines into four groups with regard to their thermal behaviour as indicated by the χ's. They are, (i) those that show very high temperature variations, having very high χ values of about 400×10^{-6}, *e.g.* 128, 207 cm.$^{-1}$; (ii) those that show medium χ value of about 100×10^{-6}, *e.g.*, 265 cm.$^{-1}$; (iii) those having low χ's of the order of 40×10^{-6}, *e.g.*, 357, 466, 695 cm.$^{-1}$; and (iv) those showing very small temperature variations, having the lowest χ values of the order of 9×10^{-6}, *e.g.*, 1160, 1220 cm.$^{-1}$

Temperature and width of the Raman lines.—At room temperature, all the Raman lines are well defined except the line at 207 cm.$^{-1}$ which exhibits considerable width. On cooling, however, all the Raman lines sharpen appreciably. At high temperatures, although all the lines broaden out, the broadening is not of the same order in all the lines. The Raman line 265 cm.$^{-1}$ for example, while showing perceptible diminution in frequency shift and having a χ value of about 100×10^{-6}, does not broaden out to the same extent as do the other low frequency lines. This behaviour is exhibited by the Raman lines 357 and 395–403 also, the latter merging into one at high temperatures. The increase in width for the individual lines at low temperature regions is very small compared to the increase at higher temperatures. This will be seen from the temperature-width curves (Figs. 4, 5 and 6) where at low temperatures, the curve tends to flatten up, the slope being greater at high temperatures, *i.e.*, $d\nu/d$T the rate of change is greater at high temperatures.

The diminution in frequency shift and increase in width of the different Raman lines are found to be of comparable order of magnitude, the latter being always greater. The variations in frequency shift and width for the individual Raman lines are of the same nature, as shown by the similarity of the shape of the curves representing these. These suggest that the two effects of temperature variation, namely the decrease in frequency shift and increase in width of the Raman lines are closely connected with each other, as indicated by Sir C. V. Raman (1947).

It is proposed to make accurate determinations of the total intensity of the Raman lines at different temperatures. The peak intensities of the lines, however, are found to decrease markedly with rise of temperature.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his valuable guidance and inspiring interest in this investigation.

Summary

The Raman spectrum of quartz has been studied at a series of nine temperatures from 85° to 685° K. Data regarding the variations in frequency shift dv, breadth and the proportional change $d \log \nu / dT$ are furnished for twelve of the important Raman lines of quartz. The proportional change is found to decrease progressively with the frequency shift of the Raman line, being highest for the low frequency lines and lowest for the high frequency ones. The temperature-frequency shift and the temperature-width curves for the individual Raman lines show similar characteristics, tending to flatten up at low temperatures and the rate of change being greater at high temperatures. The peak intensity of the Raman lines is also found to decrease markedly with rising temperature.

References

1. Landsberg and Leontowitsch .. *Zeit. f. Phys.*, 1929, **53**, 439.
2. ——— and Mandelstam .. *Ibid.*, 1929, **58**, 250; 1930, **60**, 364.
3. Brickwedde and Peters .. *Phys. Rev.* 1929, **33**, 116.
4. Ney .. *Zeit. f. Phys.*, 1931, **68**, 554.
5. Ornstein and Went .. *Physica*, 1935, **2**, 503.
6. Went .. *Doctorate thesis*, Utrecht, 1935.
7. Nedungadi, T. M. K. .. *Proc. Ind. Acad. Sci.* A, 1940, **11**, 86.
8. Venkateswarlu .. *Ibid.*, 1941, **14**, 529.
9. Raman and Nedungadi .. *Nature*, 1940, **145**, 147.
10. Raman, C. V. .. *Proc. Ind. Acad. Sci.* A, 1947, **26**, 339.

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